

PB83-165837

Acidity, Nutrients, and Minerals in Atmospheric
Precipitation Over Florida: Deposition Patterns,
Mechanisms, and Ecological Effects

Florida Univ.
Gainesville

Prepared for
Corvallis Environmental Research Lab., OR

Feb 83



U.S. Department of Commerce
National Technical Information Service

NTIS

BEGIN
FIRST
LINE OF
TEXT
HERE

• • • TYPING GUIDE SHEET

FB83-165837

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTIONS
HERE

EPA-600/3-83-004
February 1983

ACIDITY, NUTRIENTS, AND MINERALS IN ATMOSPHERIC
PRECIPITATION OVER FLORIDA: DEPOSITION
PATTERNS, MECHANISMS, AND ECOLOGICAL EFFECTS

by

Patrick L. Brezonik, Charles D. Hendry, Jr., Eric S. Edgerton,
Randy L. Schulze, and Thomas L. Crisman
Department of Environmental Engineering Sciences
University of Florida
Gainesville, Florida 32611

Grant No. 805560

Project Officer: Charles F. Powers
Environmental Research Laboratory
Corvallis, Oregon 97333

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OREGON 97333

BEGIN
LAST LINE
OF TEXT

EPA-200 (Scale)
(4-76)

PAGE NUMBER

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/3-83-004	2.	3. RECIPIENT'S ACCESSION NO. P883 165837
4. TITLE AND SUBTITLE Acidity, Nutrients, and Minerals in Atmospheric Precipitation Over Florida: Deposition Patterns, Mechanisms, and Ecological Effects		5. REPORT DATE February 1983
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Patrick L. Brezonik, Charles D. Hendry, Jr., Eric S. Edgerton, Randy L. Schulze, and Thomas L. Crisman		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Environmental Engineering Sciences University of Florida Gainesville, Florida 32611		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 805560
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Office of Research and Development Corvallis, Oregon 97333		13. TYPE OF REPORT AND PERIOD COVERED Final 9/77 - 12/79
		14. SPONSORING AGENCY CODE EPA-600/02
15. SUPPLEMENTARY NOTES Project Officer: Charles F. Powers, FTS 420-4684; 503/757-4684		
16. ABSTRACT Nitrogen deposition via bulk precipitation averaged 0.77 g/m ² ·yr (range = 0.32-1.04) at 21 sampling sites within Florida during the period May 1978 - April 1979. Comparable values for total P are 17-111 and 50 mg P/m ² ·yr. Nutrient concentrations were higher in summer than in winter. Wet-only input accounted for most of the deposition of NH ₄ and NO ₃ but dryfall was more important for organic N and TP. Statewide deposition of N and P below the loadings associated with eutrophication, but loadings exceeded mesotrophic criteria at a few agricultural sites. The acidity of Florida rainfall has increased markedly in the past 25 years; annual average pH < 4.7 now occurs over the northern two-thirds of the state. Summer rain is ~ 0.2-0.3 pH units lower than winter rain; excess sulfate levels are higher at most sites during summer. H ₂ SO ₄ accounts for about 70% of the acidity, and HNO ₃ accounts for the remainder. Local (within-state) emissions of SO ₂ seem to control the acidity of Florida rainfall. The pH in softwater lakes of north-central Florida has declined up to 0.5 units over the past 20 years; no changes were observed in similar lakes of south-central Florida. Chlorophyll <i>a</i> decreased with pH in a survey of 20 softwater lakes; the major trend in phytoplankton was a replacement of bluegreen algae by green algae in acidic lakes. Slight trends were noted in zooplankton and benthic invertebrate populations along a pH gradient, but results indicate that acidic conditions as low as pH 4.6 do not have major impacts on community structure in Florida lakes.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified
		21. NO. OF PAGES 173
		20. SECURITY CLASS (This page) Unclassified
		22. PRICE

LINE 1
LINE 2
LINE 3
LINE 4

LINE 5
LINE 6

TOP OF
IMAGE
AREA

DISCLAIMER

Although the research described in this report has been funded by the U.S. Environmental Protection Agency through grant 805560 to the University of Florida, it has not been subjected to the Agency's peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

LINE 7
LINE 8
LINE 9

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLE
AND ILLUSTRATIONS

ABSTRACT

A precipitation monitoring network consisting of 21 bulk and 4 wet/dry collectors located throughout Florida was operated over the period January 1978 - December 1979 to determine spatial and temporal trends in atmospheric deposition of acidity, nutrients, and minerals. Nitrogen deposition via bulk precipitation averaged $0.77 \text{ g/m}^2\text{-yr}$ (range = $0.32\text{-}1.04$) at 21 sampling sites within Florida during the period May 1, 1978 to April 30, 1979. Comparable values for total phosphorus (TP) are $17\text{-}111$ and $50 \text{ mg P/m}^2\text{-yr}$. Highest deposition rates occurred in agricultural areas and lowest rates in coastal and forested areas. Concentrations of nutrients were higher in summer (convective) rains than in winter (frontal) events. Wet-only input accounted for 68 and 81% of the deposition of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$, but dry fallout was more important for organic N (53% of total) and especially for TP (80% of total). Inorganic forms accounted for most of the N and P in rainfall. Statewide deposition rates of N and P are below the loading rates associated with eutrophication, but the average N loading from bulk precipitation approached the mesotrophic criterion of Vollenweider, and other N and P loadings exceeded mesotrophic loading criteria at a few agricultural sites. Whereas the atmosphere is an important source of nitrogen in nutrient budgets, it is less so for phosphorus, especially if dry fallout of locally-derived dust is not considered.

The acidity of Florida rainfall has increased markedly in the past 25 years, and concentrations of nitrate and sulfate have risen correspondingly. Annual average pH values less than 4.7 now occur over the northern two-thirds of the state, and all but the extreme southern area of the state has acidic rain. Summer rain averages 0.2-0.3 pH units lower than winter rain; excess sulfate levels are higher at most sites during summer. Sulfuric acid accounts for about 70% of the observed acidity, and nitric acid accounts for the remainder. The spatial variation in $[\text{H}^+]$ of Florida bulk precipitation was accounted for by a two variable regression model:

$$[\text{H}^+] = 6.1 + 0.54 [\text{SO}_4^{2-}]_{\text{xs}} - 0.35 [\text{Ca}^{2+}]_{\text{xs}}, R^2 = 0.75$$

where xs refers to nonmarine derived material. Ammonium and nitrate are more evenly distributed (geographically), and do not account for the observed spatial trends in acidity. Local (within-state) emissions of SO_2 (and NO_x) seem to control the acidity of Florida rainfall. The annual deposition of H^+ is about 250-500 eq./ha over interior northern Florida, or about one-third to one-half the deposition rate for H^+ over the northeastern United States.

Levels of pH in softwater lakes of north-central Florida have declined by up to 0.5 units over the past 20 years; no changes have been observed in similar lakes of south-central Florida. Aluminum levels increase with decreasing pH, but observed maximum levels ($100\text{-}150 \text{ }\mu\text{g/L}$) probably are not high enough to cause fish toxicity. Chlorophyll a decreased with pH in a survey of 20 softwater lakes; TP levels also decreased with pH, but this trend does not entirely explain the pH-chlorophyll a trend. The major change in phytoplankton populations with pH was a replacement of blue-green algae by green algae in acidic lakes. Species diversity and abundance also declined with decreasing pH, but the data set exhibited much scatter. Some trends were

BEGIN
FIRST
LINE OF
TEXT
HERE

CENTER OF
PAGE

TOP OF
IMAGE
AREA

noted in zooplankton and benthic invertebrate populations along a pH gradient, but both species composition and total abundance changes were relatively subtle. Results indicate that acidic conditions (as low as pH 4.6-4.7) do not have major impacts on community structure in Florida lakes.

DROPPED
HEAD
BEGIN
SECTION
HERE

This report was submitted in fulfillment of Grant 805560 by the Department of Environmental Engineering Sciences, University of Florida under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September, 1977, to December, 1979, and work was completed as of June, 1980.

BEGIN
LAST LINE
OF TEXT

3/8"

iv

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSIONS
FOR TABLES
AND ILLUSTRATIONS

EPA Form 2350-4 (4-80)

(PREVIOUSLY CITE EPA FORM 430)

DATE SUBMITTED

U.S. GOVERNMENT PRINTING OFFICE: 1980-800-430

TYPING GUIDE SHEET

Table of Contents

	<u>Page</u>
Abstract	iii
Acknowledgments	vi
<u>Sections</u>	
1. Summary and Conclusions	1
2. Recommendations	6
3. Introduction	8
4. Nutrient and Mineral Deposition by Rainfall	10
Historical Nutrient Data	10
Sampling Procedures and Analytical Methods	13
Results and Discussion	16
Nutrients	16
Major Minerals	30
Minor Minerals	43
5. The Acidity of Rainfall in Florida	45
Experimental Methods	45
Spatial Trends in Acidity and Related Parameters	46
Wet, Bulk and Dry Deposition of Acidic and Basic Species	64
Temporal Patterns in Precipitation Acidity	71
Sources of Atmospheric Sulfur in Florida	77
Acid Rainfall in Florida: A Perspective	79
6. Effects of Acidification on Softwater Lakes in Florida	86
Previous Studies on Effects of Acid Precipitation on Aquatic Ecosystems	86
Description of the Study Regions and Lakes	89
Sampling and Analytical Methods	98
Results of Lake Study: Water Chemistry	99
Results of Lake Survey: Biological Communities	110
Phytoplankton and Chlorophyll a	110
Zooplankton	117
Benthic Invertebrates	132
Fish	145
7. References	147
<u>Appendices</u>	
Appendix I Analytical Methods	158
Appendix II Volume Weighted Mean Concentrations and Annual Deposition Rates for Each Site During the Project Period	160

ACKNOWLEDGMENTS

We wish to thank the many graduate students and assistants who participated in the project and shared the analytical load. Special thanks to Forrest E. Dierberg (fluoride analyses; throughfall study), William Fish (nutrient and trace metal analyses), Michael Hanson (aluminum analyses; lake sampling), and Allan Hubbard and Cindy Ward (nutrient analyses; data reduction). Hugh Prentice, Jack Tuschall, and Charles Fellows were in charge of the water chemistry laboratory during various phases of the project and assisted in sample analysis. Dr. Steven Bloom of the Department of Botany provided assistance for the statistical analysis of biological data. This project would not have been possible without the cooperation of the persons who maintained our precipitation collectors and sent us rainfall samples from all over the state of Florida. We gratefully acknowledge their help:

<u>Site</u>	<u>Person</u>	<u>Affiliation</u>
Bahia Honda	Mr. Bill Green	Ranger, Bahia Honda State Park
Bradenton	Mr. Russel W. Owens	AREC-IFAS*
Belle Glade	Mr. O'Neal Akers	AREC-IFAS
Chipley	Dr. R. B. Christmas	Poultry Evaluation Center-IFAS
Clewiston	Mr. J. M. Hyder and Mr. C. Brobston	Army Corps of Engineers Corkscrew Swamp Sanctuary
Corkscrew Swamp	Dr. Michael Duever	
Fort Myers	Mr. Charles D. Hendry, Sr.	
Hastings	Mr. Louis Wallis	AREC-IFAS
Jacksonville	Mr. Jack Schabel	National Weather Service
Jasper	Mr. W. H. Davis, Jr.	City of Jasper Utility Dept.
Jay	Mr. D. T. Blackman	AREC-IFAS
Lake Alfred	Dr. Robert Koo	AREC-IFAS
Lake Apopka	Dr. C. A. Conover	AREC-IFAS
Lake Placid	Mr. David B. Johnston	Archbold Bio. Station
Lisbon	Mr. Greg Frazier	Burrell Lock
Marineland	Mr. Robert L. Jenkins	Marineland
Miami	Dr. Jackson L. Fox	
Stuart	Mr. Robert Burson	
Tallahassee	Drs. L. C. Boueres and M. O. Andreae	Florida State University
Winter Garden	Mr. Frank Dudley	Winter Garden Marina

*AREC-IFAS = Agricultural Research and Education Center of the Institute for Food and Agricultural Science, University of Florida

BEGIN
FIRST
LINE OF
TEXT
HERE

CENTER OF
PAGE

TOP OF
IMAGE
AREA

CHAPTER 1. SUMMARY AND CONCLUSIONS

The results of this project can be summarized into the following conclusions, according to the three major phases of the project: (1) atmospheric deposition of nutrients and minerals; (2) the spatial and temporal distribution of rainfall acidity in Florida; and (3) the effects of acidification on chemical and biological conditions in soft-water lakes of Florida. For details the reader is referred to Chapters 4 to 6.

ATMOSPHERIC LOADINGS OF NUTRIENTS AND MINERALS

1. Bulk precipitation is an important source of nitrogen for both terrestrial and aquatic systems. Average annual loadings of total nitrogen (TN) for 21 sampling sites in Florida ranged from 0.3 to 1.3 g/m²-yr during the two year study period, with a statewide mean of 0.72 g/m²-yr. About 70% of the nitrogen was inorganic (ammonium and nitrate) and thus readily available to plants. Deposition rates were highest in rural agricultural areas (0.88 g/m²-yr) and lowest along the coast (0.58 g/m²-yr).
2. Concentrations of all nitrogen forms in bulk precipitation were higher in summer convective showers than in winter frontal rains; statewide ratios of summer/winter concentrations ranged from 1.4 (nitrate) to 1.9 (ammonium and organic N). These results probably reflect a combination of causes: higher biogenic emissions from soils during warmer weather, greater fixation of NO₂ by lightning in summer, and more efficient washout by turbulent convective showers.
3. Wet deposition (rainfall) accounted for about 70% of the total inorganic N in bulk precipitation but only about 50% of the organic N deposition. The balance represents dry fallout of particulate nitrogen.
4. Little information is available for historical comparisons, but the data suggest that in Florida the mean concentration of inorganic N in wet-only precipitation has increased three-fold over the past 20 years.
5. In comparison with critical loading rates for lake eutrophication, the annual deposition of total N at all 24 collection sites was below the values associated with eutrophic conditions (assuming nitrogen to be the limiting nutrient). The statewide average deposition rate was about 75% of the "permissible" loading for shallow lakes suggested by Vollenweider (1968); deposition at several agricultural locations slightly exceeded the permissible criterion but none approached the eutrophic loading criterion.
6. Bulk precipitation has significant levels of total phosphorus (TP); the statewide two year average was 33 µg/L, and the mean deposition rate was 48 mg P/m²-yr. On a concentration basis, summer rains had about 1.5 times as much TP as winter rains. Land use had an important effect on atmospheric deposition rates for TP. Rural (non-agricultural) and coastal sites had the lowest rates (27 and 31 mg P/m²-yr, respectively), and agricultural sites had the highest rates (66 mg/m²-yr).

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA;
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

CENTER OF
PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD;
BEGIN
SECTIONS
HERE

7. Whereas most of the total atmospheric deposition of inorganic N and TN occurs via rainfall rather than dry fallout, the opposite is true for phosphorus. At four sites with separate wet-fall/dry-fall collectors, wet deposition accounted for an average of 63% of the deposition of TN, but only 20% of the TP. Thus, most of the phosphorus in bulk precipitation is dry fallout, presumably of wind-blown particles of dust and soil. These particles probably are large, are not transported large distances, and thus probably do not represent a source of new phosphorus for terrestrial ecosystems.

8. The statewide bulk deposition of TP is only one half the permissible loading rate for the lakes that are most vulnerable to eutrophication (shallow lakes with long hydraulic residence times). In most areas of Florida, bulk precipitation supplies only about 12-16% of the loading required to induce eutrophic conditions.

9. Sodium and chloride concentrations are highly correlated in Florida rainfall and occur at a Cl/Na ratio near that for seawater (1.8). Concentration isopleths for both ions follow the outline of the peninsula, with values increasing toward the coast. Seasalt is the major (and likely the only significant) source of these ions in Florida rainfall.

10. Average total sulfate concentrations in rainfall ranged from about 0.2 to 1.2 mg/L (as S); about two-thirds of the total deposition of sulfate was by rainfall. Deposition rates ranged from 3 to 23 kg S/ha-yr (for all sites over the two years), indicating that the atmosphere serves as a significant source of sulfur to soils in Florida.

ACIDITY OF PRECIPITATION

1. Rainfall throughout Florida is acidic, with average values for all but a few stations in south Florida being less than geochemical neutrality (pH~5.7). Single events as low as pH 3.9 were measured at Gainesville, and the lowest pH of a bulk precipitation sample (collected weekly or biweekly) was 3.73 (at Jay in the western panhandle during August, 1978).

2. A definite geographic pattern exists for acid deposition in the state; mean annual pH values (volume-weighted) for 1978-79 were around 4.6-4.7 throughout the panhandle and northern two-thirds of the peninsula. Mean annual values south of Lake Okeechobee were around 5.0 or above.

3. Neutralization of bulk precipitation was found for coastal sites, but wet-only precipitation collected near both the Gulf and Atlantic coasts was approximately as acidic as inland stations of comparable latitude. Partial neutralization of acidity in coastal rain apparently results from dry deposition of alkaline particles containing calcium carbonate of local (terrestrial) origin. Analysis of the ionic composition of coastal bulk precipitation indicates that sea spray is not the agent of neutralization. Sea-salt sulfate levels were only modestly elevated compared to inland bulk precipitation, and the calculated amount of sea-salt calcium carbonate is too low to account for the neutralization.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA;
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

BEGIN
FIRST
LINE OF
TEXT
HERE

CENTER OF
PAGE

TOP OF
IMAGE
AREA

4. A seasonal pattern was found in precipitation acidity throughout the state, with summertime pH averaging 0.2-0.3 units lower than wintertime values. Possible reasons for the difference include (1) increased summertime emissions of SO_2 and NO_x (caused in part by seasonal demands for air conditioning), (2) greater thunderstorm activity in summer, resulting in greater fixation of NO_x by lightning, (3) enhanced scavenging efficiency of summer convective showers compared to winter frontal storms, and (4) differences in the frequency and size of individual rain events between summer and winter. Further studies are needed to evaluate the importance of some of these factors.

5. Granat-type analysis indicates that about 70% of the rainfall acidity in Florida is derived from sulfuric acid and 30% from nitric acid. A multiple regression equation with $[\text{H}^+]$ as the dependent variable and $[\text{SO}_4^{2-}]_{\text{xs}}$ and $[\text{Ca}^{2+}]_{\text{xs}}$ as independent variables explained about 75% of the variance in hydrogen ion concentration over the statewide network. The sub-script xs refers to the fraction of the ions of non-marine origin. Thus the pH of rainfall in Florida primarily reflects the degree to which sulfuric acid has been neutralized by terrestrial calcium carbonate.

6. Bulk precipitation throughout northern and central Florida deposited 250-500 equiv H^+ /ha-yr during 1978-79, which is about one-third to one-half of the annual deposition of H^+ in the heavily impacted northeastern United States. Comparable values for excess sulfate are 7-11 kg/ha-yr in northern Florida and ~13 kg/ha-yr in the northeastern U.S. (10 year average for Hubbard Brook, N. H.). Thus Florida ecosystems receive 50-90% of the excess sulfate from the atmosphere as their northern counterparts.

7. Although historical data are lacking on the pH of Florida rainfall, calculated values for rainfall pH during the mid-1950's indicate wet-only precipitation was not acidic then. Moreover, present values of sulfate deposition in northern Florida are up to four times higher than values for the early 1950's. Scattered information for the pH of rainfall at Gainesville from 1973 to the present, however, do not show any long term trends.

8. In spite of the north-south gradient of decreasing rainfall acidity, long-range (interstate) transport of acid precursors is not a wholly satisfactory explanation for acid precipitation in Florida. A substantial portion of the H_2SO_4 and HNO_3 must be derived from in-state emissions of SO_2 and NO_x , which are widespread and substantial. These conclusions are supported by several lines of evidence, including the fact that summer rainfall throughout the entire state is more acidic than winter rainfall. From a meteorological viewpoint, peninsular Florida is isolated from the rest of the United States during summer. Large-scale weather patterns for the peninsula come from the southeast (Caribbean) or southwest (Gulf of Mexico) during summer, and cold fronts from the north rarely penetrate the state during this period.

EFFECTS OF ACID PRECIPITATION ON FLORIDA LAKES

1. A large number of soft-water lakes occur in the sand-hill highlands region of peninsular Florida. Based on comparison of historical and current data for 12 such lakes in northern Florida and 8 soft-water lakes in south-

3/8"

3

central Florida, pH has decreased by up to about 0.5 units in many of the northern soft-water lakes, whereas no temporal trends could be discerned for the southern group. The northern (Trail Ridge) lakes lie about 40-50 km east of Gainesville in a region receiving rainfall with a (volume-weighted) average annual pH of 4.5-4.7. The southern (Highlands Ridge) lakes lie northwest of Lake Okeechobee, near the current southern terminus of pronounced rainfall acidity. Corresponding decreases in alkalinity and increases in sulfate concentration were observed in the northern lakes.

2. The 20 lakes surveyed had annual average pH levels ranging from 4.72 to 6.80, but otherwise had generally similar characteristics (soft water, oligotrophic to mesotrophic nutritional conditions). The group thus served as a good data base to evaluate the effects of acid precipitation on vulnerable aquatic ecosystems in Florida.

3. A general trend of increasing aluminum with decreasing pH was found in the 20 Florida lakes. However, maximum values (100-150 $\mu\text{g/L}$) were below the levels associated with fish toxicity; this may explain the occurrence of largemouth bass and several other common game fish species in lakes with pH values below 5.0.

4. A general trend of increasing chlorophyll a concentration with increasing pH was found. However, total phosphate concentration also tended to rise with pH. The trend of greater oligotrophic conditions in more acidic lakes may be caused by lower rates of nutrient cycling at lower pH, or it may reflect watershed nutrient loading factors that just happened to correlate with lake pH. Further studies are need on this point.

5. The number of phytoplankton species and their abundance in a lake decreased with increasing acidity, but much scatter occurred for both parameters. Although the data are fairly limited, a trend of increasing phytoplankton abundance with increasing pH was found for a series of lakes with similar levels of phosphate. The lake survey also indicated that species composition varied along a pH gradient, with green algae replacing blue-greens at low pH. In lakes with pH values of 4.5-5.0, 60% of the algae were green (Chlorophyta), and 25% were blue-green (Cyanophyta). Corresponding values for lakes in the pH range 6.5-7.0 were 31% green algae, 63% blue-green algae.

6. Similar trends were found in the zooplankton, i.e. a significant decrease with pH; the trend exhibited considerable scatter. In general, the number of zooplankton species found at a given pH was greater than the number found in temperate lakes of comparable pH. Six species of zooplankton were dominant at all pH levels, and five other species were always present but never dominant. Two types of multivariate analysis (principal component and cluster analysis) showed that the zooplankton populations could be grouped along pH gradients, but the population differences with pH are relatively subtle. Rare species showed greater differences with pH than did common species.

7. No clear trends were seen in either the diversity or the abundance of benthic invertebrates with pH, and the differences that were found among the

lakes may reflect differences in trophic conditions more than direct effects of pH.

8. Limited information has been obtained on fish populations in acidic Florida lakes. No species replacement or disappearance trends were found. Condition factors relating weight and length indicated that the fish in acidic lakes are in poorer condition than those in less acidic lakes, possibly reflecting the decreased availability of food in acidic lakes. Breeding populations are still being maintained in the most acidic lakes. No evidence of gill necrosis was found in any fish, reflecting the relatively low concentrations of aluminum in the lakes.

CHAPTER 2. RECOMMENDATIONS

This project has resulted in a thorough characterization of the role of atmospheric precipitation as a source of nutrients and minerals. The assembled data base will be useful as a benchmark for future conditions and as input to local and regional-scale nutrient budgets. A few questions remain unresolved with regard to atmospheric sources of nutrients, and further work should address these.

The size distribution of atmospheric phosphate particles should be determined, and work should be done to characterize the chemical form of phosphate in these particles. This information will be useful to clarify questions regarding the atmospheric residence time of suspended phosphate and the distance that such particles travel in the air. Such information is necessary to determine whether the enhanced collection of phosphate in bulk precipitation (compared to wet-only precipitation) represents a new (external) source of phosphate for a given site or merely is part of an internal cycle of wind-induced suspension and particle deposition in the immediate vicinity of a bulk precipitation collector.

Regarding atmospheric deposition of nitrogen, further studies should focus on rates of gaseous depositions (i.e. NH_3 and NO_2 uptake by plant, soil and water surfaces). These processes were found to make large contributions to a mass balance model of nitrogen in peninsular Florida (Messer and Brezonik 1980, 1981). This model calculated gaseous deposition using literature values for deposition velocities and measured levels of these gases in the atmosphere of Florida. Direct measurements of NH_3 and NO_2 deposition need to be done under a variety of meteorological conditions and for a variety of land use and vegetation types. Such work is difficult and time-consuming, but it is necessary to evaluate the model calculations. Further measurements of ambient NH_3 and NO_2 concentrations in rural and coastal areas are needed to refine model calculations.

The acidity of rainfall in Florida has been well documented by this project (e.g. Brezonik et al. 1980). Continued monitoring of pH and associated parameters in rainfall should be undertaken using a smaller network of sampling stations around the state. Such information is needed to determine temporal changes in the severity of the problem at a given site and to determine changes in geographic distribution (e.g. the spread further southward of rainfall acidity). Because Florida's population is still increasing at a rapid rate, demands for electric power and fossil fuel consumption are increasing more rapidly than in most other states. The shift to coal-fired power plants that is occurring in Florida (as in the rest of the United States) is further reason for the continued careful monitoring of rainfall. The source of acidity in Florida precipitation has not been resolved completely, although evidence presented in this report indicates that emissions of SO_2 and NO_x within the state are largely responsible. Large-scale modeling and field measurement studies on acid precursors will be needed to refine estimates of long-distance transport into the state.

The lake studies conducted as part of this project have described the effects of increased acidity on community structure in softwater lakes.

BEGIN
FIRST
LINE OF
TEXT
HERE

CENTER IN
PAGE

TOP OF
IMAGE
AREA

Further studies should emphasize the effects of pH changes on metabolic processes--nutrient cycling and productivity in these lakes. The effects of acidification on fish populations need to be quantified. Reasons for the relatively low concentrations of aluminum in acidic Florida lakes should be determined. Virtually nothing is known about the effects of acid rainfall on the sandy, poorly-buffered soils commonly occurring in Florida. Studies should be undertaken on the effects of acid rainfall on soil chemistry and soil microbiology. Effects of acid precipitation on agricultural crops in Florida (e.g. citrus, pine forest, vegetables, sugar cane) should be studied. This work should focus on direct effects of air-borne acid impacting on the foliage and fruit of such vegetation during various phases of their growth cycle and indirect effects that could occur with soil acidification. Finally, holistic watershed-level studies need to be undertaken to determine the relationship between acidic inputs to the poorly buffered soils of Florida and the movement of acidity-related substances into lakes and streams.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSIONS
FOR TABLES
AND ILLUSTRATIONS

CHAPTER 3. INTRODUCTION

The chemistry of rainfall has been studied for over a century, but many questions remain about its importance in biogeochemical cycles and in transport of pollutants from the atmosphere to terrestrial and aquatic ecosystems. Because the nitrogen cycle involves several volatile or gaseous compounds, the importance of atmospheric reactions and transfers in this cycle has been recognized for a long time. Measurements of the inorganic N content of rainfall date back to the late 19th century. Much less information is available on levels of organic N and other "rock-bound" nutrients (e.g. phosphorus) in rainfall. Moreover, information in the literature exhibits a wide variation in concentrations both spatially and temporally in rainfall. Causes for this variability have not been explained.

The role of rainfall as a transport mechanism for various pollutants such as heavy metals and acidity has been recognized in recent years, and a considerable volume of data has been assembled on the pH of rainfall in Scandinavia and the northeastern United States. The deleterious effects of acid rainfall on aquatic systems in temperate climates also has been documented. Analysis of geographic and long-term temporal trends in acid precipitation indicates that acid precipitation is a potentially very serious environmental problem of international magnitude. Previous acid rainfall studies in the United States have been skewed geographically to the Northeast, where the problem apparently is most severe. Little information is available on the extent of the problem in other areas, such as the Southeast. Edaphic conditions in this region, and especially in Florida, suggest a high susceptibility for deleterious ecological effects, and demographic patterns suggest that this region may experience increasingly acidic precipitation in the future.

Information on the role of other atmospheric deposition processes, namely particulate and gas deposition, in nutrient and pollutant transport is much less definitive. The project that this report summarizes was undertaken to evaluate the role of atmospheric deposition processes in the transport of nutrients, minerals, and certain pollutants (primarily acidity) to the earth's surface.

Most of the project results are based on two large scale field studies. The first, a statewide sampling network for bulk and wet-only precipitation, was used to evaluate the importance of rainfall and dryfall as sources of nutrients, minerals, and acidity to Florida eco-systems. The network was established to allow analysis of the influence of surrounding land-use patterns on deposition rates of these substances. Samplers were located in urban, agricultural, forested, coastal, and pristine areas, and transects were established to evaluate north-south and east-west (coastal-inland) gradients in deposition patterns. Details of the sampling procedures and results are presented in Chapters 4 and 5. The network provided valuable information on nutrient and mineral deposition patterns (Chapter 4), and yielded the first comprehensive analysis of the acid rainfall problem in the state of Florida (Chapter 5).

The second field effort involved a sampling program on 20 softwater lakes in north-central and south-central Florida. Routine limnological measurements

and complete chemical and biotic analyses, were done on each lake to evaluate the effects of acidification. Phytoplankton, zooplankton and benthic invertebrate communities were analyzed for species diversity and abundance. Results of the lake studies are presented in Chapter 6.

Two other aspects of atmospheric deposition processes were studied during this project but are not presented in this report. The importance of gas (NH_3 and NO_2) deposition in the cycling of nitrogen was evaluated by means of a mass balance model of nitrogen in peninsular Florida. The results of this model are presented elsewhere (Messer and Brezonik 1980, 1981), and they imply that these processes are major sources of nitrogen to terrestrial and aquatic ecosystems in Florida.

The trace heavy metal content of bulk precipitation and within-storm variability of heavy metal levels in rainfall also were determined during this project, and deposition patterns were determined for various heavy metals in sediments of ten lakes sampled as part of the survey on acidification effects. Results of the trace metal studies are being assembled for a thesis and will be published separately.

CHAPTER 4. NUTRIENT AND MINERAL DEPOSITION BY RAINFALL

The primary purpose of this phase of the study was to evaluate the role of precipitation as a source of nutrients to aquatic and terrestrial ecosystems in Florida. Emphasis was placed on nitrogen and phosphorus forms, but all major minerals were measured, and results are presented here for deposition of mineral ions, as well. A number of studies have reported on the chemical composition of precipitation in Florida; however, most of the studies had limited objectives and involved only a few parameters, a few sampling locations, or short sampling periods. Comprehensive data on the chemical composition of rainfall in Florida thus are lacking. The most important previous studies are described below.

HISTORICAL NUTRIENT DATA

Junge (1958) and Junge and Werby (1958) reported on the major ion content (including NH_4^+ and NO_3^-) of (wet-only) rainfall collected during 1955-56 at four Florida locations (Tallahassee, Tampa, West Palm Beach, and Jacksonville), as part of a nationwide study of precipitation chemistry. A second national sampling network (Lodge et al. 1968) existed from 1960 to 1966 and reported data on major ions, inorganic N, and trace metals in wet-only precipitation at Tampa.

The nutrient content (i.e. N and P forms) of Florida rainfall has been measured by a number of investigators in various locations over the past decade, primarily in relation to efforts to determine nutrient budgets for lakes. Brezonik et al. (1969) measured inorganic and organic N and P in bulk precipitation during 1968 at a rural site 40 km east of Gainesville and computed atmospheric loadings to several isolated, pristine lakes in that area. Nutrient budget studies (Joyner 1971) on Lake Okeechobee, the largest lake in Florida, yielded data on bulk precipitation collected near the lake during 1969.

Nutrient budget and mineral cycling studies on a mixed hardwood forest (Ewel et al. 1976) and cypress wetlands (Bourne 1976; Hendry 1977) included nutrient measurements on rainfall in the north central Florida area. Gaggiani and Lamonds (1978) and Burton et al. (1978) studied the effects of highway construction on nutrient inputs to lakes in Orlando and Tallahassee, and both studies included nutrient measurements on rainfall. Lamonds and Merritt (1976) determined the nutrient content of bulk precipitation at two sites along the proposed cross-Florida Barge Canal (central Florida) during 1975. Mattraw and Sherwood (1977) conducted urban runoff studies at Fort Lauderdale and reported nutrient analyses of rainfall collected in that area. Finally, rainwater samples were collected over South Florida during the 1973 Florida Area Cumulus Experiment (Wisniewski and Cotton 1974) both at the ground surface and by aircraft at the cloud-base level (600 m). The historical data on nutrients in Florida precipitation are summarized in Table 4-1; in general, the various studies show considerable variability. Because of the large number of locations and short sampling periods involved in these studies, it is difficult to infer trends. However, recent data for wet-only precipitation indicate that there has been a substantial (three-fold) increase in inorganic N levels compared to those found 25 years ago (Junge 1958).

Table 4-1. Summary of historical data on nutrient content of Florida rainfall.

Reference	Collection Period	Locations(s)	Sampler Type ¹	NH ₄ ⁺ -N	NO ₃ ⁻ -N	TIN	TON	Constituent, µg/L	SRP	Total P
Junge (1958)	1955-56	Tallahassee W. Palm Beach Jacksonville	W	40	50	90				
Lodge et al. (1968)	1960-66	Tampa	W			80				
Brezonik et al. (1969)	1968	rural north-central Fla.	B	80	120	200	180	380	12	29
Joyner (1971)	1969	Moore Haven	B	260	120	380	310	690	23	40
Schneider et al. (1969)	1969	Winter Garden	B	180	180		160	430		59
Ewel et al. (1976)	1971-73	rural north-central Fla.	B						100	
Wisniewski and Cotton (1978)	1973	rural south Fla. South Fla. Miami	B C B	150 230 280	150 180 260	300 410 540				
Gaggiani and Lamonds (1978)	1972-74	Orlando	B	640	340	980	560	1540	100	140
Bourne (1976)	1974	Gainesville	B	200	100	300	250	150	50	150
Mattraw and Sherwood (1977)	1974-75	Fort Lauderdale	B	120	270	390	130	520	17	26
Burton et al. (1978)	1974-75	Tallahassee	B W	170 110	290 190	460 300			17 5	37 29

Table 4-1. (Con't)

Reference	Collection Period	Location(s)	Sampler Type ¹	NH ₄ ⁺ -N	NO ₃ ⁻ -N	TIN	TON	TN	SRP	Total P
Lamonds and Merrit (1976)	1975	Central Fla.	B	310	210	520	390	910	35	50
Hendry and Brezonik (1980)	1977-79	Gainesville	B	120	230	350	470	820	24	85
			W	100	190	290	410	700	19	34
Ranges			B	80-640	90-340	200-980	160-560	380-1540	12-100	29-140
			W	40-110	50-190	80-300			5-19	29-34

¹ B = Bulk; W = Wet-only; C = Cloud.

SAMPLING PROCEDURES AND ANALYTICAL METHODS

Precipitation Monitoring Network.

In order to assess the regional variations in atmospheric fluxes of nutrients to lakes and soils, a statewide precipitation monitoring network was established in fall of 1977. The network consisted of 24 collection stations from Jay in the panhandle near Pensacola, to Bahia Honda in the lower Keys. The locations of the sampling sites in the Florida Atmospheric Deposition Network (FADN) are shown in Figure 4-1. Table 4-2 gives the county in which each station is located, its coordinates and starting date of operation.

The large number of collection sites permit interpretation of the rainfall data in terms of various demographic, land-use, and geographic parameters. Urban and semi-urban sites are represented by Miami, Gainesville, Tallahassee, Jacksonville, and Fort Myers. Rural sites in predominantly forested areas include Bronson, Lake Placid, Corkscrew Swamp, and Waldo. A number of sites are in areas of intensive agriculture: Hastings (potato farms); Lake Alfred, Lake Apopka (citrus); Bradenton (vegetables); Belle Glade, Clewiston (sugarcane); Chipley (chicken farm); and McArthur Farms (dairy cattle). Coastal stations include Cedar Key, Marineland, Stuart, and Bahia Honda Key. Three collection transects were organized within the state so that the distribution and trends in rainfall chemistry could be studied. One transect extended the length of the peninsula from Jasper, near the Georgia border to Belle Glade, south of Lake Okeechobee. A second transect was established east-west across the northern part of the state (Marineland to Cedar Key), and a third transect consisted of a series of collectors (east-west) across South Florida (Stuart to Ft. Myers), with a clustering of sites around Lake Okeechobee. Many of the FADN stations were located at and operated in conjunction with University of Florida agricultural research stations that collect climatological data. Twenty-one stations had collectors designed for bulk precipitation (Likens 1972), and four were equipped with automatic Aerochem-Metrics Model 101 wet/dry collectors that collected the wet and dry fractions separately. The Gainesville station had both a wet/dry and a bulk collector. Samples were collected bi-weekly at 20 of the sites either by us or by technicians at the research stations, who measured the rainfall amount over the collection period and mailed the samples to our lab for analysis. Samples at three stations (Jay, Jacksonville, and Miami) were collected weekly, and samples at Gainesville were collected on an event basis. Dryfall samples were collected by adding 300 mL of deionized water to the bucket and scrubbing the bucket with a clean plastic glove to dislodge particulates. Analyses were then run on the rinsings.

Analytical Methods.

Analytical methods for chemical determinations of the precipitation and dryfall samples are summarized in Appendix 1. In general, analyses were performed according to Standard Methods (APHA 1976) and/or the EPA water analysis manual (U.S. EPA 1976). Inorganic nitrogen forms (NH_4^+ , NO_2^- , NO_3^-), chloride, and sulfate were determined by automated methods on a Technican AutoAnalyzer; soluble reactive phosphate (SRP, roughly equivalent to ortho-phosphate) was determined manually with a Beckman Model DBG spectrophotometer.

3/8"



Figure 4-1. Location of sampling stations in the Florida Atmospheric Deposition Study Network.

Table 4-2. Location of Stations in the Florida Atmospheric Deposition Study Network.

Station	County	Coordinates	Starting Date
Apopka	Orange	81°30' 28°40'	7/77
Bradenton	Manatee	82°30' 27°30'	3/78
Belle Glade	Palm Beach	80°40' 26°45'	12/77
Bahia Honda	Monroe	81°10' 24°40'	11/77
Bronson	Levy	82°45' 29°30'	12/77
Chipley	Washington	85°30' 30°50'	4/78
Cedar Key	Levy	83°0' 29°10'	12/77
Clewiston	Hendry	81°0' 26°45'	12/77
Corkscrew	Collier	81°40' 26°30'	1/78
Fort Myers	Lee	81°50' 26°45'	11/77
Gainesville	Alachua	82°20' 29°30'	7/76
Hastings	St. Johns	81°30' 29°45'	11/77
Jacksonville	Duval	81°45' 30°30'	8/78
Jasper	Hamilton	82°50' 30°30'	4/78
Jay	Santa Rosa	87°10' 30°45'	4/78
Lake Alfred	Polk	81°50' 28°10'	1/78
Lake Placid	Highlands	81°30' 27°10'	12/77
Lisbon	Lake	81°45' 28°50'	3/77
MacArthur	Okeechobee	80°40' 27°20'	1/78
Miami	Dade	80°15' 25°50'	11/77
Marineland	Flagler	81°10' 29°40'	11/77
Stuart	Martin	80°15' 27°10'	4/78
Tallahassee	Leon	84°15' 30°30'	1/78
Waldo	Alachua	82°15' 29°40'	4/78

¹ All stations were sampled until fall of 1979. A modified network consisting of 12 stations sampled weekly was in operation during 1980.

BEGIN
FIRST
LINE OF
TEXT
HERE

CENTER OF
PAGE

TOP OF
IMAGE
AREA

and 4-cm cell, using the single reagent colorimetric method. Total Kjeldahl nitrogen (TKN) and total phosphate (TP) were determined by manual (semi-micro) digestion in test tubes, followed by colorimetric analysis for ammonium (Auto-Analyzer) and orthophosphate (manually) on the neutralized digestate. Cation analyses were done by flame atomic absorption spectrophotometry following procedures recommended in the instrument manual (Varian 1973). Quality assurance/quality control procedures are discussed on page 16a.

DROPPED
HEAD,
BEGIN
SECTIONS
HERE

RESULTS AND DISCUSSION

Introduction

Solute concentrations generally are inversely related to the quantity of rainwater falling during a storm. Computing volume-weighted average concentrations tends to equalize the importance of light rains, having relatively high concentrations, and heavy rains, in which constituents are more dilute. Volume-weighted concentrations were calculated by:

$$C_j = \frac{\sum_{i=1}^n C_{ij} V_i}{\sum_{i=1}^n V_i}$$

where C_{ij} = concentration (mg/L) for the j^{th} constituent in i^{th} rain sample, and V_i = rainfall amount (cm) in a sampling period.

Summary results of statewide volume-weighted mean concentrations and loadings for major ions and nutrients in bulk precipitation are presented in Table 4-3. Volume-weighted mean concentrations of all parameters at each site and annual depositions are given in Appendix 2. Annual loading rates were calculated by multiplying the volume-weighted concentration for each constituent by the total rainfall over the given time period.

The period, May 1978 through April 1979, represents the first full year during which the entire (FADN) sampling network was in existence; thus this period (hereafter referred to as the intensive year) was selected for detailed discussion in this report. As shown by Table 4-3, the values of mean concentrations and loadings for this period are close to those found over the entire 2 year study. The month of May also represents the beginning of the summer (rainy) season in Florida, and consequently May is a convenient starting point for an annual study.

Nutrients

Results on atmospheric deposition of nutrients are presented in six sections: (1) geographical variation of atmospheric fluxes of N and P; (2) speciation of N and P forms in precipitation; (3) seasonal variations in the nutrient content of rain; (4) relative importance of dry fallout and wet deposition as sources of nutrients; (5) comparisons of present concentrations and fluxes with historical data; and (6) examination of the significance of atmospheric nutrient deposition relative to critical loading rates for lake eutrophication.

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUS-
TRATIONS

QUALITY ASSURANCE/QUALITY CONTROL

Quality Assurance/Quality Control (QA/QC) on the project consisted of specific methodologies and checks that were performed as an integral part of the field sample collection procedures, laboratory analytical schemes, and data management processes.

Field Collection QA/QC -- Collection of precipitation and dryfall samples involved both bulk and wet/dry collection systems. Collection system blanks consisted of distilled, deionized water aliquots passed through the funnel and tubing of the bulk collectors and added to clean buckets of the wet/dry collectors. These system blanks were routinely checked for pH and conductivity, and periodically processed through the complete analytical scheme to ensure that cleaning procedures for the collection equipment were adequate and that the cleaning procedures did not introduce contaminants to the samples. Replication between the bulk and wet/dry collectors was evaluated by co-locating a bulk and wet/dry sampler at the Gainesville site. In this manner, total deposition as measured by both types of collectors was evaluated. Results of the co-located samplers are described in subsequent sections. Chain-of-custody control on sample and field data (i.e., rainfall deposition amounts and collection interval dates) included field labeling of samples with unique site names and codes that were then recorded in the project notebook upon receipt of samples from the field.

Laboratory QA/QC -- Upon receipt at the laboratory, samples were aliquoted and batched into field groups on a weekly basis. Each field group was then processed through the complete analytical scheme. Included with the field groups were sample replicates and EPA Reference Standards. The pH and conductivity of a dilute, mineral acid solution ($5 \times 10^{-5} \text{N H}_2\text{SO}_4$) was checked, prior to sample analysis, in order to monitor ionic strength effects of the electrodes. Routine QA/QC procedures of the Department of Environmental Engineering Sciences Water Chemistry Laboratory included the use of analytical grade chemicals for all analytical reagents, performing instrumental calibrations, response checks, and standardizations for each analytical run, and analyzing instrumental blanks and EPA Reference Standards.

Data Management QA/QC -- Data from instrumental recorder strip charts were entered into the project notebook and then keypunched onto computer cards. Random checks of data entries on the computer printouts were performed by tracing values back to the original strip charts. Computer checks were performed on cation/anion balances and calculated vs. measured specific conductance to assess overall quality and completeness of the analytical regime.

Table 4-3 Statewide mean Concentrations and Loadings by Bulk Precipitation for Various Periods during the Two Year Study.

Study Period	5/78-4/79		Calendar 1978		Calendar 1979		Total Study 1978 + 1979	
Number of Samples	595		531		603		1,134	
Number of Bulk Sites	22		21		22		21	
Parameter	Conc. ¹	Loading ²	Conc.	Loading	Conc.	Loading	Conc.	Loading ³
Na	1.18	1.49	1.06	1.17	1.37	1.99	1.19	1.58
K	0.21	0.28	0.22	0.27	0.18	0.25	0.18	0.26
Mg	0.16	0.20	0.15	0.17	0.19	0.27	0.16	0.22
Ca	0.65	0.86	0.59	0.72	0.62	0.87	0.58	0.80
SO ₄ ²⁻	1.81	2.45	1.90	2.43	1.69	2.54	1.75	2.49
Cl ⁻	2.21	2.80	2.05	2.27	2.55	3.71	2.27	2.99
NH ₄ ⁺ -N	0.18	1.24	0.21	0.27	0.14	0.22	0.17	0.25
NO ₃ ⁻ -N	0.20	0.27	0.23	0.29	0.18	0.27	0.20	0.28
TON	0.17	0.23	0.18	0.23	0.14	0.21	0.16	0.22
SRP	0.026	0.034	0.030	0.038	0.016	0.022	0.021	0.030
TP	0.038	0.050	0.045	0.057	0.029	0.042	0.036	0.050

¹ Volume-weighted mean concentration; all values are mg/L.

² Loading rates are g/m²-yr

³ Average annual loading over the two-year period.

1. Geographical Variation of Nutrient Deposition

Nitrogen. Deposition of TN by bulk precipitation at the 21 sites during the intensive year ranged from 0.32 g N/m²-yr at Bahia Honda Key to 1.04 g N/m²-yr at Belle Glade (Figure 4-2A). The Bahia Honda site represents an almost completely maritime regime, while the Belle Glade site is located in the Everglades Agricultural Area, a large area of sugarcane plantations and vegetable farms. Mean deposition of TN over all 21 sites was 0.77 g N/m²-yr. The statewide mean deposition of TN for calendar year 1978 was 0.80 g/m²-yr, and the corresponding mean for 1979 was 0.63 g/m²-yr.

Based on then existing literature, Brezonik (1976) concluded that bulk deposition of TN ranges from 1.0 to 2.0 g/m²-yr over large area of the United States, and that deposition rates outside the range of 0.5 to 3.0 g/m²-yr are likely to occur only under unusual circumstances. Deposition rates across Florida fall in this range (Figure 4-2), except at two pristine sites, Bahia Honda Key and Corkscrew Swamp (0.45 g/m²-yr), a remote Audubon sanctuary, located in the Big Cypress Swamp in south Florida.

Table 4-4 summarizes the mean deposition of TN for groups of the stations classified according to dominant land-use in the immediate area. Deposition rates were lowest at coastal and non-agricultural rural locations; highest loadings occurred at sites in dominantly agricultural regions. The latter sites received about 50% more loading of TN than did the coastal sites.

Phosphorus. Deposition of TP by bulk precipitation in Florida during May 1978 - April 1979 (Figure 4-2B) ranged from 17 (Bahia Honda Key) to 111 mg P/m²-yr (Jasper), with 51 mg P/m²-yr as the mean for all sites. The site at Jasper is in an area of phosphate mining, and the observed high deposition rate may reflect dust from mining activities. The statewide mean deposition rates for TP in calendar 1978 and 1979 were 57 and 42 mg/m²-yr. Thus average deposition of both TN and TP was lower in 1979 than in 1978, although the amount of rainfall actually was about 11% higher in the latter year. In general, highest deposition rates were recorded at agricultural locations, and lowest rates occurred at rural and coastal sites (Table 4-4). Atmospheric deposition of TP at the former sites was more than double that at the latter sites. According to Chapin and Uttormark (1973), atmospheric phosphorus fluxes usually range from 0.1 to 1.0 kg/ha-yr (10 to 100 mg/m²-yr); the results in Figure 4-2B fall in this range, except for the value for Jasper.

2. Nitrogen and Phosphorus Speciation

Nitrogen. In both wet-only and bulk precipitation nitrogen was predominantly present in inorganic forms (NH₄⁺ and NO₃⁻). The statewide mean concentrations for TIN in bulk precipitation for 1978, 1979, and the intensive year were 0.43, 0.36 and 0.38 mg/L respectively (about two thirds of the TN content), and the mean content of TIN in wet-only samples at the four wet/dry sites for the period May 1978 - April 1979 was 0.28 mg/L (68% of the TN). Most network sites exhibited the concentration sequence NO₃⁻ > NH₄⁺ > TON (Figure 4-3A); averaged over all sites concentrations were 0.20, 0.18, and 0.17 mg N/L, respectively, during the intensive year. Several agricultural sites, however, had higher levels of NH₄⁺-N than of NO₃⁻-N. The highest (volume



Figure 4-2. (A) Total nitrogen deposition (gN/m²-yr) and (B) Total phosphorus deposition (mg P/m²-yr) in bulk precipitation across Florida, May, 1978 to April, 1979. At sites equipped with wet/dry collectors the sum of the wet and dry deposition is shown.

Table 4-4. Deposition of total nitrogen and total phosphorus at stations grouped according to dominant land use in the area.¹.

	TN g/m ² -yr	TP mg/m ² -yr
Coastal	0.58	31
Urban	0.76	50
Rural (non-agricultural)	0.62	27
Rural (agricultural)	0.88	66
State	0.75	51

¹. Results are for the year: May 1978-April 1979.

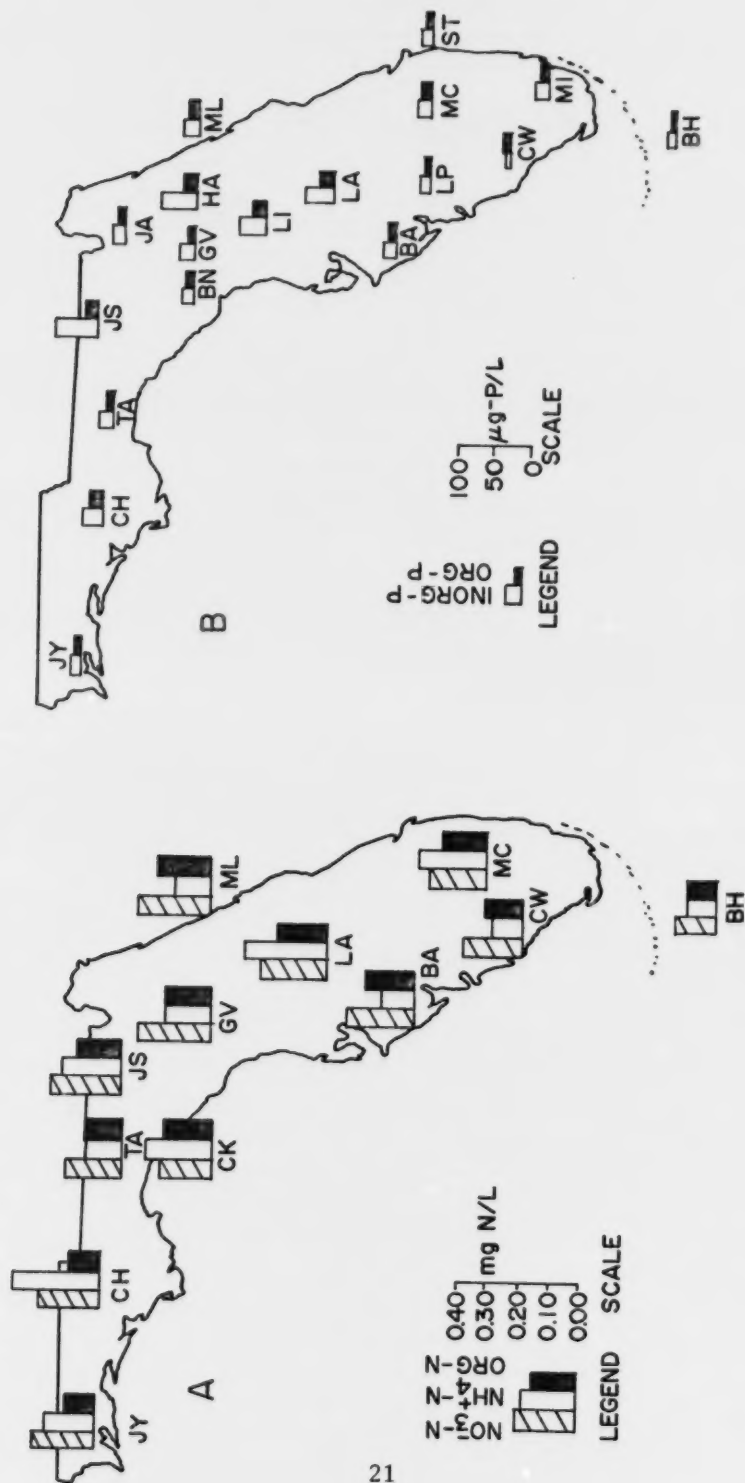


Figure 4-3. (A) Volume-weighted average concentrations of NO_3^- , NH_4^+ , and organic nitrogen and (B) Volume-weighted average concentrations of inorganic and organic phosphorus in bulk precipitation. For clarity, not all sites are shown.

weighted) mean concentration of $\text{NH}_4^+\text{-N}$ (0.34 mg/l) and largest difference relative to $\text{NO}_3^-\text{-N}$ were recorded at Chipley. This station is located at an agricultural research station, and a large poultry farm (50,000 chickens) is located near the site.

Phosphorus. SRP was the dominant form of phosphorus in both bulk and wet-only precipitation. The state-wide mean concentrations of SRP for 1978, 1979, and the intensive year were 27, 13, and 26 $\mu\text{g/L}$, respectively, or about 68% of the TP content. Organic P had mean concentration of 12 $\mu\text{g/L}$ averaged over all the bulk collection sites for the same three time periods. Wet-only concentrations of SRP and organic P were much lower: 5 $\mu\text{g/L}$ and 3 $\mu\text{g/L}$, respectively, averaged over the four collection sites (for the intensive year). Figure 4-3B illustrates the volume-weighted mean concentrations of inorganic and organic P in bulk precipitation across Florida. At all the sites except Corkscrew Swamp, concentrations of SRP were greater than those for organic P, and highest concentrations were found at sites located in predominantly agricultural regions or in areas of phosphate strip mines.

3. Seasonal Variations in the Nutrient Content of Precipitation

Nitrogen. Rainfall in Florida generally follows a bimodal seasonal pattern, with most of the rain occurring in the summer and winter months. Summer rainstorms are convective events; winter rains generally are associated with cold fronts moving down the peninsula. Spring and fall generally are dry seasons; thus it is convenient to compare Florida rainfall chemistry on a summer/winter basis. The summer values are for the months of May to October, while the winter values are for November to April. As shown in Table 4-5, concentrations of both inorganic and organic N are greater in summer (convective) rain storms than in winter (frontal) events. Averaged over all sites, ammonium and TON concentrations in summer rains were almost double the winter levels, and NO_3^- and TN were 40 and 70% higher, respectively. The greater concentrations in summer rain may have resulted from three factors: increased biogenic emission of gaseous N compounds due to higher summer soil temperature; N_2 fixation by lightning, which frequently is associated with summer storms; and/or more efficient washout of substances in the highly turbulent convective storms.

Plots of monthly average concentrations of NO_3^- and NH_4^+ in bulk precipitation do not show such pronounced seasonal trends as might be expected from the summary data in Table 4-5. Figure 4-4 shows monthly variations in these ions and monthly amounts of rainfall at three sites across the state: Jay (northwest corner), Gainesville (north central peninsula), and Miami (southeast Florida). Although concentrations at Jay (Figure 4-4A, and Gainesville (Figure 4-4B) were higher during summer than winter, highest concentrations occurred in samples collected during spring and fall when there was little rain. These high values likely reflect atmospheric buildup of contaminants during dry periods. A seasonal (summer/winter) pattern is not discernible at subtropical Miami (Figure 4-4C), where highest concentrations occurred during driest months.

Phosphorus. As shown in Table 4-5, volume-weighted average concentrations for SRP and organic P are 60 and 70% higher, respectively, in summer compared to winter. Monthly plots of SRP and TP for Jay and Gainesville

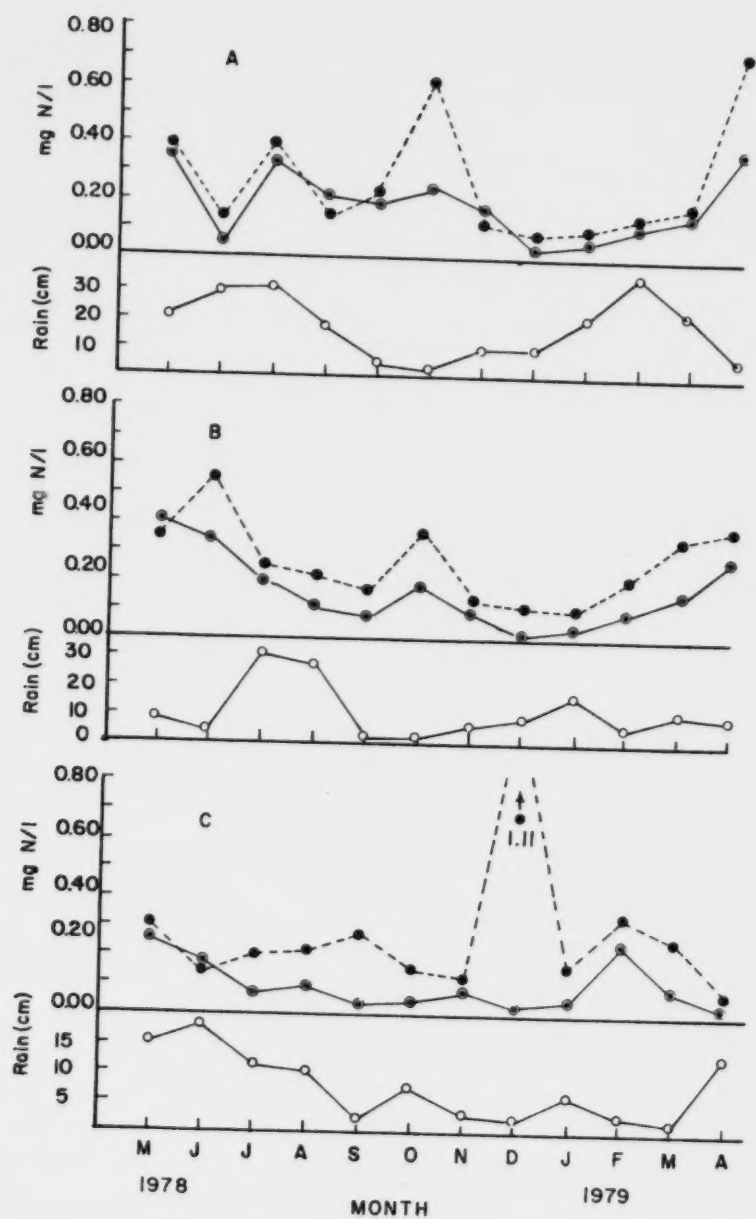


Figure 4-4. Monthly volume-weighted mean concentrations of NH_4^+ (solid line), NO_3^- (dashed line), and rainfall at Jay (A), Gainesville (B), and Miami (C) from May, 1978 to April, 1979.

Table 4-5. Statewide annual and summer/winter (volume-weighted) mean concentrations of nitrogen and phosphorus in bulk precipitation.¹

	Annual	Summer	Winter	Ratio: $\frac{\text{Summer}}{\text{Winter}}$
	mg/L			
NH ₄ ⁺ -N	180	230	120	1.9
NO ₃ ⁻ -N	200	230	160	1.4
ORG N	170	210	110	1.9
TN	550	670	390	1.7
SRP	26	32	20	1.6
Org P	12	15	10	1.5
TP	38	47	30	1.6

¹. Results are for the year: May-October 1978(summer); November 1978 - April 1979(winter).

(Figure 4-5A and B) show a pronounced decline in concentrations of SRP and TP during the winter months (Dec., Jan., Feb.). However, the levels of SRP and TP at Miami (Figure 4-5C) were greatest during these months. As was true for N species, the driest months generally had the highest concentrations of both SRP and TP.

4. Comparison of Wet vs. Dry Deposition of Nutrients

Nitrogen. Wet/dry collectors yield information concerning the mechanism of deposition for nutrients. Table 4-6 summarizes results for wet and dry deposition of TN at the four sites with wet/dry collectors. Mean deposition of TN by wet-only input over all four sites was approximately double the average dryfall input. The highest total deposition occurred at Belle Glade, while the coastal site at Cedar Key had the lowest TN deposition of the four sites. The sampler at Belle Glade generally collected the largest amounts of particulate matter among the four sites, especially during fall and winter, when nearby sugarcane fields were burned prior to harvesting. At these times, the dryfall collector had noticeable amounts of black soot.

The partitioning of N between wet and dry fallout in Table 4-7 shows that wet-only input averaged 81 and 68%, respectively, of the total deposition of NH_4^+ and NO_3^- . Thus for these two substances, rainfall was the predominant deposition mechanism. Atmospheric precursors of NH_4^+ and NO_3^- in rainwater are gases (NH_3 and NO_x) and secondary aerosols (particulates formed by gaseous reactions, e.g. NH_4NO_3 , NH_4HSO_4). These aerosols are very small ($<1 \mu\text{m}$) and thus do not settle from the atmosphere as dryfall. They are hygroscopic, however, and as a result they are important as condensation nuclei for rain drop formation.

While wet-only input is the major mechanism for inorganic N deposition, it is less important for the input of organic N; only 47% of the average atmospheric input of organic N was from wet deposition. At Gainesville and Cedar Key, ca. 60% of the TON deposition was by wet input, while at Apopka and Belle Glade, TON deposition via wet input was only about 35%. As discussed above, the Apopka and Belle Glade sites are located in areas of intensive agriculture, and atmospheric deposition in these areas seems to reflect activities such as plowing and harvesting that introduce relatively large (hence rapidly settling) particles into the atmosphere. Dryfall of soil-derived particles thus appears to be an important mechanism for organic nitrogen input, while rainfall is more important for deposition of inorganic nitrogen.

Phosphorus. Wet and dry deposition of phosphorus at the four wet/dry sites is summarized in Tables 4-6 and 4-7. The Belle Glade collector recorded the highest (wet plus dry) deposition of TP ($96 \text{ mg/m}^2\text{-yr}$), while the coastal Cedar Key collector measured the least deposition ($24 \text{ mg/m}^2\text{-yr}$). The mean (wet plus dry) deposition of TP for the four collectors was $59 \text{ mg/m}^2\text{-yr}$ (Table 4-6).

Dryfall input of phosphorus was more important than wet precipitation, accounting for 80% of the total deposition averaged over the four sites (Table 4-7), and the reverse was true for nitrogen. Only 15% of the organic P (operationally defined here as TP minus SRP) was deposited via rainfall, while 27%

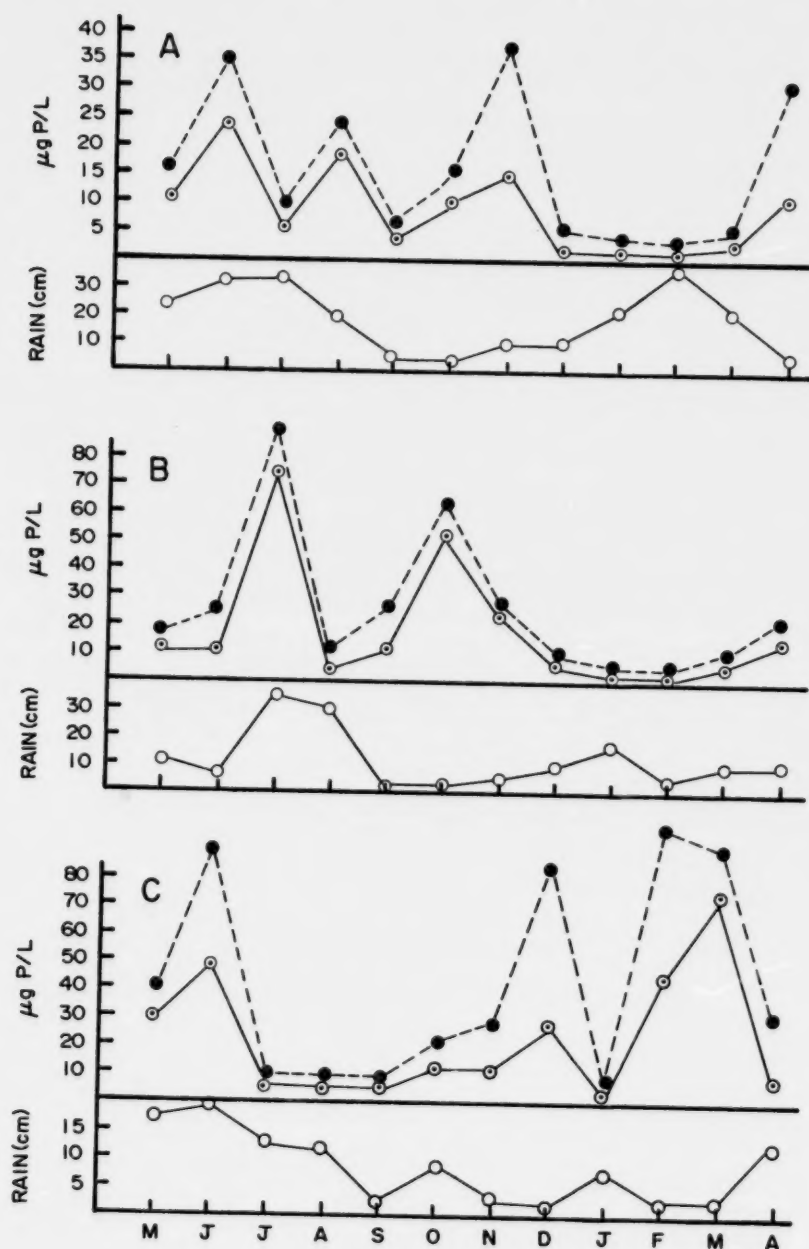


Figure 4-5. Monthly volume-weighted mean concentrations of SRP and TP at Jay (A), Gainesville (B) and Miami (C) from May, 1978 to April, 1979.

Table 4-6. Wet and dry deposition of total nitrogen and phosphorus at sites with wet/dry collectors.¹

Site	Total Nitrogen (g/m ² -yr)			Total Phosphorus (mg/m ² -yr)		
	Wet	Dry	Total	Wet	Dry	Total
Gainesville	0.63	0.28	0.91	16	42	58
Cedar Key	0.52	0.25	0.77	6	18	24
Apopka	0.47	0.34	0.81	9	48	57
Belle Glade	0.64	0.49	1.13	12	84	96
mean	0.57	0.34	0.91	11	48	59

¹•Results are for the year May 1978-April 1979.

Table 4-7. Relative deposition of nitrogen and phosphorus forms by wet versus total (wet plus dry) deposition at the four wet/dry collection sites.*

Location	NH ₄ ⁺	NO ₃ ⁻	TIN	Org N	TN	SRP	Org P	TP
Gainesville (urban)	88	70	74	59	69	40	19	28
Cedar Key (Coastal)	82	62	69	61	68	33	20	25
Apopka (agric.)	70	74	72	33	58	20	11	16
Belle Glade (Agric.)	83	67	72	38	57	15	9	13
Average	81	68	72	48	63	27	15	20

*Values are % deposition by "wet-only" precipitation = (100 x loading from wet collector)/total loading (wet plus from dry).

Values are for the year May 1978-April 1979.

of the SRP was from rainfall. Deposition of TP at the agricultural Belle Glade site was 87% via dryfall and only 13% by rain (Table 4-7). Since phosphorus is a nonvolatile element, its cycle generally is limited to rock-soil-water phases. Atmospheric deposition of phosphorus, therefore, primarily reflects gravitational settling of relatively large particles that enter the atmosphere by such activities as agriculture, mining, and fires. The high dryfall deposition of TP (relative to wet input) at the two agricultural locations demonstrates the importance of land-use activities on atmospheric deposition of terrigenous substances.

5. Historical Comparison

Historical data are available for the wet-only deposition of TIN to compare with the present data. Chapin and Uttormark (1973) constructed an isopleth map of TIN flux using Junge's (1955-56) data for ammonium and nitrate in wet-only precipitation. The map shows a TIN flux of 0.10 to 0.15 g/m²-yr across the southeastern U.S., including Florida. TIN fluxes via wet-only precipitation measured in this study ranged from 0.3 to 0.44 g/m²-yr, with a mean of 0.39 g/m²-yr. The annual mean TIN concentration averaged over Junge's four Florida sites (1955-56) was 0.09 mg/L, and Lodge et al. (1968) found a volume-weighted mean TIN concentration of 0.08 mg N/L in wet-only precipitation at Tampa during the period 1960-66. Although there have been numerous studies of bulk precipitation across Florida since 1966, only two wet-only investigations have been reported (Table 4-1). Burton et al. (1978) found 0.30 mg/L TIN in wet-only precipitation during 1974-75 at Tallahassee, while Hendry and Brezonik (1980) reported 0.29 mg/L TIN in Gainesville wet-only precipitation (1976-77). Averaged over the 4 wet-only collections sites in the present (FADN) study, the TIN concentration was similar to the above values (0.28 mg N/L); thus the mean concentration of inorganic nitrogen in wet-only precipitation and the corresponding flux have increased about three-fold in Florida over the last two decades.

TIN in bulk precipitation averaged 0.38 mg/L over all FADN sites, ranging from 0.28 (Corkscrew) to 0.59 (Chipley) mg/L. Historical data (Table 4-1) for TIN in bulk precipitation in Florida range from 0.20 to 0.98 mg/L. With such large variability, no historical trends can be inferred concerning the levels of TIN in bulk precipitation. Fewer data are available for TON levels in Florida precipitation (Table 4-1), and the values again show a wide range, 0.16 to 0.56 mg/L. The state-wide mean (all sites) for TON in this study was 0.17 mg/L, which is near the low value of the above range.

Average total phosphorus (TP) concentration was 38 µg/L for all FADN bulk precipitation sites, with a range of 29 to 59 µg/L for individual sites. Previous studies (Table 4-1) have reported a wide range (29-140 µg/L) of values at various locations over the last ten years. As mentioned earlier, this large variation likely is due to differing local conditions and short (< 1 yr) sampling periods.

6. Significance of N and P Loadings Relative to Lake Eutrophication

The atmospheric loading rates of TN and TP at each bulk precipitation site can be examined in the context of critical nutrient loading rates for

BEGIN
FIRST
LINE OF
TEXT
HERE

CENTER OF
PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD.
BEGIN
SECTIONS
HERE

lake eutrophication. Figure 4-6 illustrates the relationship between the bulk loading rates of N and P at each site during the intensive year and the critical loading rates developed by Vollenweider (1968, 1975). The state-wide mean (averaged over all the sites) deposition rate is also shown in the figure. For both N and P, the statewide mean rates are below the "permissible" values defined by Vollenweider. However, the rates at several predominantly agricultural sites do exceed the "permissible" levels. While atmospheric inputs of N and P by themselves would not produce the water quality problems generally associated with lake eutrophication, the higher deposition rates may support substantial standing crops of phytoplankton. Moreover, the mean loading rate for nitrogen from bulk precipitation is about 75% of the total "permissible" loading and about 37% of the nitrogen loading rate associated with the onset of eutrophic conditions.

Thus even rather low contributions of nitrogen from surface water sources may be sufficient either to make nitrogen non-limiting or to induce eutrophic conditions, assuming nitrogen were the limiting nutrient. The above calculations also do not consider the atmospheric nitrogen inputs from gaseous absorption or from rainfall that reaches a lake via runoff in the watershed; for further discussion of these aspects see Messer and Brezonik (1981). The high rates of nitrogen deposition from the atmosphere, coupled with the relative mobility of nitrogen (compared to phosphorus) in terrestrial systems, help to explain why nitrogen seldom is observed to be the limiting nutrient in lakes.

For phosphorus the situation is somewhat different. The statewide mean loading is half the permissible rate for lakes that have a q_s (areal water loading rate) = 1 m/yr, and only one fourth of the permissible loading for lakes with q_s = 5 m/yr. Most Florida lakes have q_s values < 5 m/yr. Figure 4-6 suggests that atmospheric deposition alone supplies only about 12 to 16% of the loading required to cause eutrophic conditions in Florida lakes.

Major Minerals

1. Sodium, Chloride and Sulfate

Volume-weighted average concentrations of sodium and chloride concentrations are plotted in Figure 4-7A and 4-8A. The concentration isopleths for both Na^+ and Cl^- , roughly follow the outline of the peninsula. This is not surprising since the source of the NaCl in rain and dryfall across Florida is the Atlantic Ocean and Gulf of Mexico. In fact, the Cl^-/Na^+ ratios in bulk precipitation (Figure 4-7B) across the state are close to the ratio of these ions in seawater (1.8). Sites with ratios less than 1.8 indicate Na^+ enrichment, while ratios greater than 1.8 indicate Cl^- enrichment relative to sea salt. The mean ratio of the state (22 sites) is 1.83. The concentration isopleths (Figure 4-7A and 4-8A) are more closely spaced on the west than east coast of the state, indicating a sharper concentration gradient. The east coast (Atlantic) is a high-energy coastline and salt particles are carried farther inland than is the case along the west coast and panhandle.

The input of NaCl appears rather constant over time. Junge and Werby (1958) reported Na^+ concentrations at Jacksonville and Tampa of 0.96 and 0.63

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

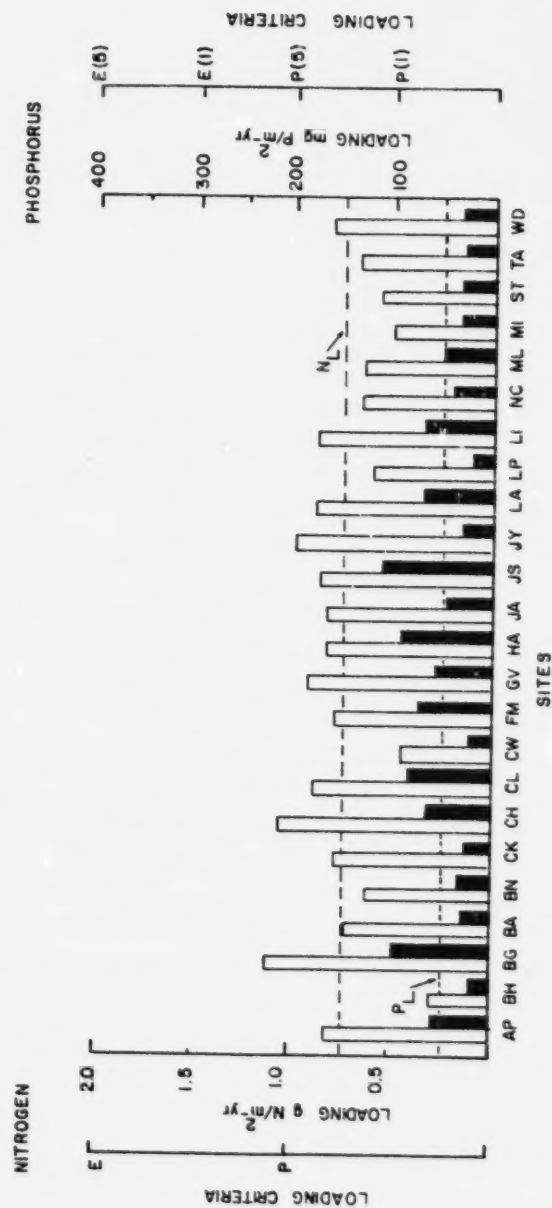


Figure 4-6. Loadings of nitrogen (open bars) and phosphorus (closed bars) by bulk precipitation at each sampling site. Statewide average loadings shown by dashed lines. Permissible (P) and Excessive (E) loading criteria for nitrogen are for lakes with mean depth $< 5\ m$ (Vollenweider 1968). Loading criteria for phosphorus are for two values of areal water loading ($q_s = 1$ and $5\ m/yr$) as given by Vollenweider (1975).

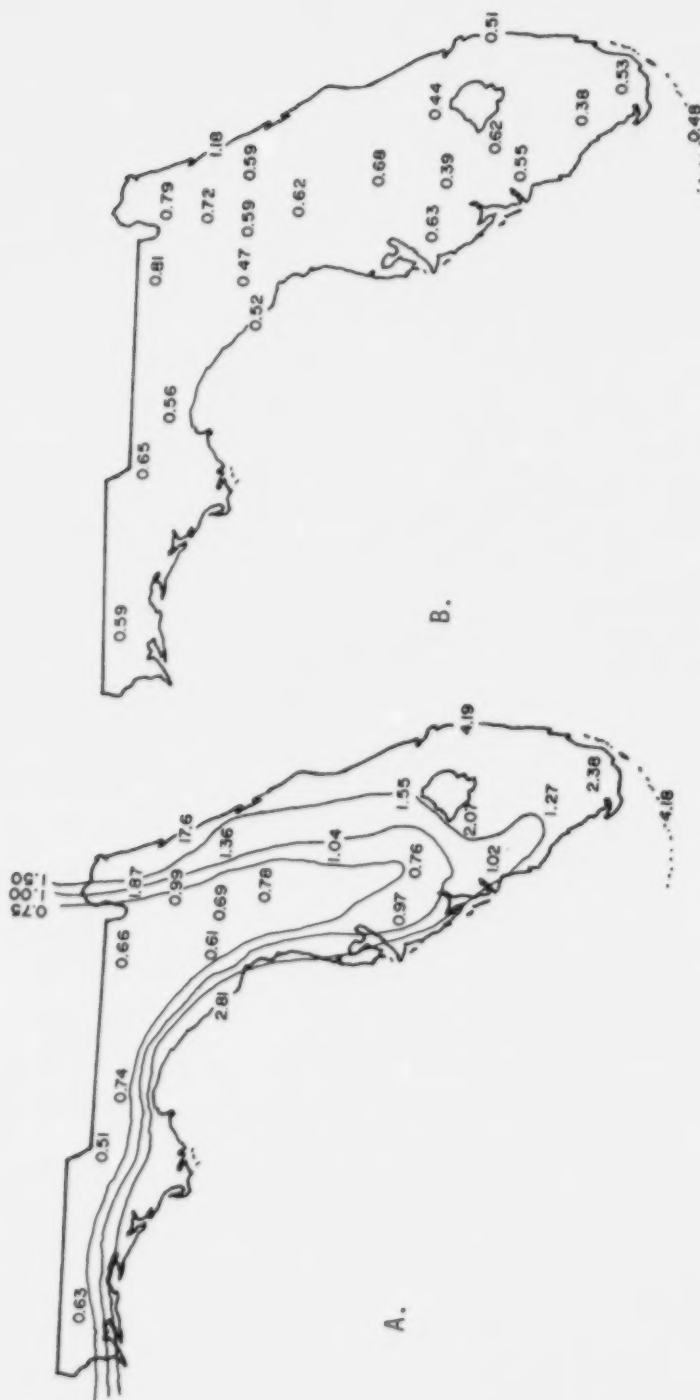


Figure 4-8. Volume-weighted mean concentrations of (A) chloride and (B) sulfate (as sulfur) in bulk precipitation in Florida, May 1978 - April 1979. All concentrations in mg/L.

BEGIN
FIRST
LINE OF
TEXT
HERE

CENTER OF
PAGE

TOP OF
IMAGE
AREA

mg/L, respectively for 1955-56. Sodium concentrations at FADN sites (Jacksonville and Bradenton) near the earlier sampling locations were 1.08 and 0.51 mg/L, respectively.

DROPPED
HEAD
BEGIN
SECTION
HERE

Sulfate (SO_4^{2-} -S) concentrations in bulk precipitation during the intensive year (Figure 4-8B) ranged from 1.18 (Marineland) to 0.38 mg/L (Corkscrew Swamp). Over the two year period (1978 and 1979) for all sites sulfate-S concentrations ranged from 0.31 to 1.48 mg/L. Sulfate in rainfall originates from three sources: (1) marine-derived sulfate from sea-salt aerosols, (2) biogenic emission to the atmosphere and subsequent oxidation of reduced sulfur compounds (H_2S , dimethyl sulfide, dimethyl disulfide), and (3) anthropogenic emission of sulfur compounds (SO_2 , particulate SO_4^{2-}). Sulfate deposition was principally by wet processes (average of about 75% of the total deposition (Table 4-8), with dry deposition rates higher during winter than summer (Table 4-9). The importance of wet versus dry deposition, the relative importance of the above sources for sulfate in Florida precipitation, and the relationship of sulfate to rainfall acidity are discussed in greater detail in Chapter 5.

2. Calcium, Magnesium and Potassium

Highest levels of calcium generally were recorded in the southern half of the state (Figure 4-9A). Calcareous deposits (limestones) in this area are located just a few feet below the surface of the top soil, and they outcrop in some areas south of Lake Okeechobee. Mining of these deposits for use in concrete manufacturing is extensive in south Florida.

Calcium in rainwater arises mainly from terrestrial sources; i.e. the ocean provides only small amounts of Ca^{2+} to the atmosphere; this matter is discussed further in Chapter 5 relative to the factors affecting rainfall acidity in Florida. As a result of the terrigenous origin, isopleth patterns for Ca are not similar to those for Na^+ and Cl^- . Although the highest volume-weighted average concentrations of Ca^{2+} in bulk precipitation occurred at Marineland on the Atlantic coast (Figure 4-9A), calcium derived from sea-salt accounted for only about 0.34 mg/L of the total Ca^{2+} concentration; i.e. 1.30 mg/L is "excess" calcium. The high level of Ca^{2+} in rain at this site is likely due to a combination of wave-action on outcroppings of coquina (limestone) rock along the coast and wind-driven suspension of calcareous particles in coastal soils. A high "excess" Ca^{2+} (0.72 mg/L) also was recorded at the maritime site, Bahia Honda in the lower Keys (Figure 4-9). This excess Ca undoubtedly arises from the limestone rock which forms the archipelago of the Florida Keys. Calcium and the associated carbonate-bicarbonate species are important parameters controlling the acidity (pH) of precipitation in south Florida. The pH of Florida rain results from interaction of atmospheric acids (H_2SO_4 and HNO_3) with terrestrially-derived bases (e.g. CaCO_3); see chapter 5 for a detailed discussion.

In general, magnesium levels in bulk precipitation (Figure 4-9B) correlate with both calcium concentrations (Figure 4-9A) and sodium concentrations (Figure 4-7a). Highest Mg^{2+} levels were found at the southern sites, and high values also were measured for coastal locations. Sea salt supplies a substantial proportion of the Mg^{2+} in precipitation at coastal locations. In fact, all the magnesium in rain at the four coastal sites (Cedar Key, Bahia

BEGIN
LAST LINE
OF TEXT

3/8"

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLES
AND ILLUSTRATIONS

Table 4-8. Wet and dry deposition of minerals at the wet/dry collection sites.¹

	Gainesville			Cedar Key			Apopka			Belle Glade		
	g/m ² -yr		% by wet	g/m ² -yr		% by wet	g/m ² -yr		% by wet	g/m ² -yr		% by wet
	Wet	Dry		Wet	Dry		Wet	Dry		Wet	Dry	
Sodium	0.35	0.24	59%	1.96	0.48	80%	0.40	0.33	55%	0.59	0.47	56%
Chloride	0.67	0.46	59%	3.63	0.82	82%	0.77	0.53	59%	1.22	0.99	55%
Calcium	0.38	0.67	36%	0.47	0.40	54%	0.32	0.31	51%	0.70	1.71	29%
Magnesium	0.06	0.07	46%	0.25	0.08	76%	0.06	0.06	50%	0.08	0.15	35%
Potassium	0.12	0.06	67%	0.14	0.06	70%	0.10	0.15	40%	0.15	0.20	43%

¹ Values are for the year May 1978 - April 1979.

Table 4-9. Dry Deposition of Minerals on a (Summer/Winter) Seasonal Basis.¹

Deposition Rate, g/m²-yr

Location	Na ⁺	Cl ⁻	Ca ⁺²	Mg ⁺²	K ⁺	SO ₄ ^{-2-S}
Gainesville						
Winter	0.27	.051	0.69	0.07	0.06	0.25
Summer	0.19	0.40	0.57	0.09	0.06	0.25
Cedar Key						
Winter	0.57	1.00	0.41	0.09	0.06	0.14
Summer	0.25	0.65	0.32	0.06	0.06	0.12
Apopka						
Winter	0.37	0.58	0.39	0.07	0.13	0.19
Summer	0.33	0.53	0.21	0.05	0.11	0.14
Belle Glade						
Winter	0.56	1.18	1.95	0.18	0.23	0.31
Summer	0.33	0.71	1.53	0.10	0.14	0.18

¹ Values are for the year May 1978 - April 1979.



Figure 4-9. Volume-weighted mean concentrations of (A) calcium and (B) magnesium in bulk precipitation in Florida, May 1978 - April 1979. All concentrations in mg/L.

Honda, Stuart, and Marineland), is derived from seasalt (Mg/Na in seawater is 0.12).

Potassium arises in rainfall principally from soil-derived particles. Concentrations of K^+ were highly variable over the bulk precipitation sites (Figure 4-10), and they seem to reflect nearby land-use activities. Lowest average concentrations were found at the two most pristine locations (Lake Placid and Corkscrew Sanctuary), while higher levels were recorded at agricultural locations (Clewiston, Hastings).

3. Wet and Dry Deposition of Minerals

The relative importance of wet vs. dry input of minerals is summarized in Table 4.8. Sodium and chloride deposition at all four wet/dry sites occurred primarily by wet-only input. Atmospheric sea-salt particles are highly hygroscopic and serve as condensation nuclei for rain drop formation. No simple trend in deposition mechanism can be seen for Ca^{2+} , Mg^{2+} , and K^+ , and either wet or dry processes dominated depending on the site. For example, at the highly-agricultural Belle Glade site, total deposition of all three metals was largely by dry fall (Table 4-8), but at Apopka and Cedar Key, wet and dry deposition of Ca^{2+} was about equal. A strong seasonal-dependence was found in the dry deposition of the five minerals (Table 4-9), with dryfall input during the winter months being greater than that in the summer. This trend likely reflects a lower frequency of rain events during that season compared to the summer rainy season.

4. Comparison of Wet Plus Dry and Bulk Deposition Rates for Major Minerals.

Two different types of collectors (i.e. wet/dry and bulk) were employed in the precipitation network, and it is of interest to determine whether the wet plus dry deposition rates (from the wet/dry collectors) correspond to the bulk deposition rates for various species. Assuming that wet deposition did not vary with collector type, two questions are raised regarding dry deposition. The first involves collector height; bulk collectors in the network were located 2 m above ground and wet/dry collectors were ~1 m above the ground. If a concentration gradient in atmospheric particulates exists between 1 and 2 m, then there may be a difference in deposition between the two collectors.

The second question involves shape: bulk collectors are conical, while the wet/dry collectors are cylindrical. The flow of air around the two collectors is different, and thus the rate of turbulent deposition also may differ. This problem is not completely distinct from that of reference height, because wind speed and eddy diffusivity are functions of height. However, the intent here is simply to point out the gross differences between collectors and then to determine whether these differences might be responsible for inconsistent deposition rates.

Adequate data are available at two sites (Gainesville and Orlando) to compare adjacent wet/dry and bulk collectors, and deposition of major cations and anions in the two types of collectors are summarized in Table 4-10. Generally, the agreement between wet/dry and bulk collectors is acceptable.

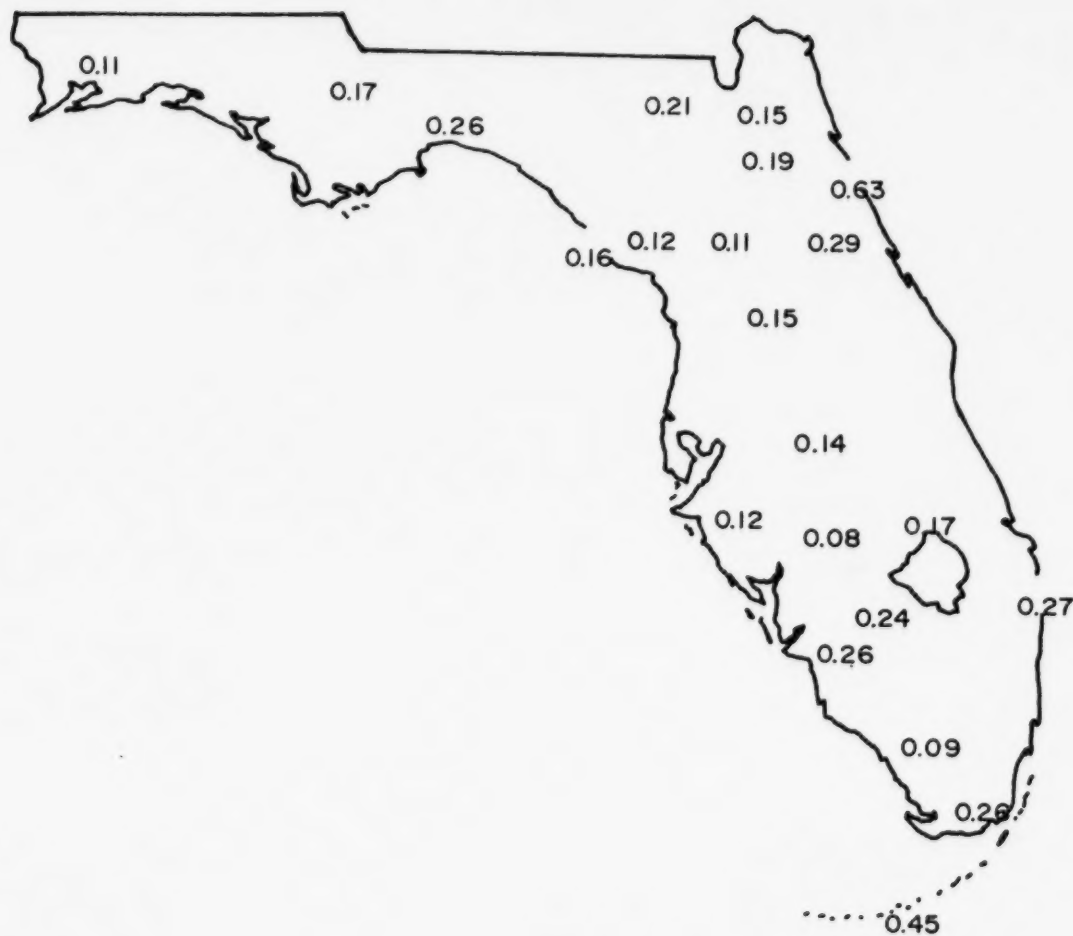


Figure 4-10. Volume-weighted concentrations of potassium in bulk precipitation across Florida (May 78 - May 79). All values are mg/L.

Table 4-10. Comparison of loading rates of major ionic species as determined by wet/dry and bulk precipitation collectors.¹

Location	Annual Deposition (kg/ha)								
	H ⁺	Na ⁺	K ⁺	Ca ⁺²	Mg ⁺²	NH ₄ ⁺ -N	NO ₃ ⁻ -N	excess SO ₄ ⁼	Cl ⁻
Gainesville									
Wet + Dry	0.24	5.79	1.65	10.0	1.43	1.85	3.55	24.5	11.3
Bulk	0.27	5.25	1.58	8.5	1.15	2.33	3.44	24.4	10.0
<u>Wet + Dry</u> x 100	89	110	104	118	124	80	103	100	113
Bulk									
Orlando									
Wet + Dry	0.19	7.43	2.00	6.18	1.20	1.52	3.16	23.7	13.3
Bulk	0.22	6.71	2.07	5.49	0.71	1.97	3.18	23.8	10.1
<u>Wet + Dry</u> x 100	86	111	97	113	169	77	99	100	132
Bulk									

¹. Values are for the year May 1978-April 1979.

BEGIN
FIRST
LINE OF
TEXT
HERE

CENTER OF
PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD
BEGIN
SECTIONS
HERE

Deposition of sulfate and nitrate, which both originate as gases or sub-micron particles, was the same in both types of collectors at the two sites. Deposition of H^+ and NH_4^+ was lower in both wet/dry collectors than in nearby bulk collectors. The difference in H^+ deposition reflects large cation excesses (hence by inference, alkalinity) in the dry bucket. The wet deposition of H^+ alone was higher in both cases than the bulk deposition. In calculating the total loading from wet/dry collectors, the alkalinity was assumed to titrate a stoichiometric amount of H^+ . The ammonium discrepancy is unexplained, but may signify either a positive gradient in the vertical direction or simply differences in NH_3 interaction with the two collector surfaces.

Deposition rates of Ca^{+2} and Mg^{+2} were consistently higher for the wet/dry collectors than the bulk collectors. This may reflect the difference in collector heights and the occurrence of a concentration gradient of suspended soil species near the ground. Assuming that most of the Ca^{+2} and Mg^{+2} deposited in the collectors was associated with carbonate, the excess of these ions in the wet/dry collectors, relative to the bulk collectors, explains the observed underestimate of H^+ deposition in the wet/dry system.

Sea-salt (Na^+ and Cl^-) deposition also was higher in the wet/dry collector. Although this could be due to association of $NaCl$ with soil particles, this would necessitate a relatively high percentage of Na^+ and Cl^- in soil dust. This is unlikely, considering the different solubilities (leaching rates) of terrestrially-derived and oceanic species. The fact that deposition of most particulate species was higher in the wet/dry collectors suggests that the shape and height of the bulk sampler may contribute to turbulent scouring of the funnel and thus to low deposition rates.

Despite the aforementioned differences between the wet/dry and bulk deposition rates, the results are generally comparable. Most species were deposited to the two collectors with less than 20% difference, and for several species differences were only a few percent. Unless sampling requirements are very stringent, it seems that either collector will yield an adequate description of atmospheric deposition. Furthermore, deposition patterns are reflected in a consistent manner by the collectors. Both collectors indicate that H^+ deposition at Gainesville was higher than that at Orlando, while Na^+ , Cl^- and K^+ deposition was higher at Orlando than Gainesville. The problems associated with deposition of particulate species may be overcome, or at least diminished, by adjustment of collector height and by careful selection of sampling location.

5. Comparison of Bulk Precipitation and Throughfall.

Bulk precipitation at the Waldo site, 10 km NE of Gainesville, was collected atop a 20 m (65 ft) steel tower which extended through the top of the forest canopy. Concurrent with these collections, throughfall also was collected at the base of the tower, below the tree canopy. As shown in Table 4-11, distinct chemical differences were found between the bulk precipitation and throughfall. On an annual, volume-weighted average basis, throughfall contained elevated concentrations of all chemical species except H^+ and NH_4^+-N . On a seasonal basis, differences in concentration between the two types of samples were relatively small during summer (May 1978 - Oct. 1978),

BEGIN
LAST LINE
OF TEXT

BOTTOM OF
IMAGE AREA
OUTSIDE
DIMENSION
FOR TABLE
AND ILLUSTRATIONS

Table 4-11. Comparison of major ions, conductivity, and nutrients in bulk precipitation and throughfall on an annual and a summer/winter basis at the Waldo site.¹

	μg/L	Annual		Summer		Winter	
		Bulk	Throughfall	Bulk	Throughfall	Bulk	Throughfall
H ⁺		24 (pH 4.62)	19 (pH 4.73)	32 (pH 4.49)	18 (pH 4.74)	16 (pH 4.80)	19 (pH 4.72)
Specific Conductance	μmho/cm	18.1	29.9	10.7	19.7	15.4	42.3
Na	mg/L	0.59	1.57	0.51	0.71	0.67	2.60
K	mg/L	0.20	0.59	0.30	0.52	0.09	0.67
Mg	mg/L	0.08	0.33	0.06	0.19	0.09	0.67
Ca	mg/L	0.30	1.34	0.31	0.83	0.28	1.96
SO ₄ ²⁻	mg/L	2.15	3.18	2.31	2.88	1.99	3.55
Cl ⁻	mg/L	0.99	3.24	0.69	1.02	1.31	5.94
NH ₄ ⁺ -N	mg/L	.144	.121	.094	.054	.197	.202
NO ₃ ⁻ -N	mg/L	.202	.219	.231	.232	.170	.203
TON	mg/L	0.24	0.34	0.30	0.32	0.17	0.37
SRP	mg/L	.014	.017	.021	.019	.007	.015
TP	mg/L	.025	.030	.041	.039	.009	.019

¹ Values are for the periods May - October 1978 (summer) and November 1978 - April 1979.

and nutrient concentrations were approximately the same in the two sample types. Concentrations found in the winter months (Oct. 78 - Apr. 78), however, were much higher in throughfall than in bulk precipitation (except for H^+). This likely reflects the fact that the leaves on the trees (primarily cypress, *Taxodium distichum*) die in the late fall and minerals are more easily leached from the leaf tissue. Ewel et al. (1976) found increased mineral levels (Ca, Mg, K, and P) in both throughfall and stemflow compared to bulk precipitation collected in a north Florida mixed hardwoods forest, and they attributed the higher levels to leaching of the plant tissue. Ewel et al. also reported higher levels of the four minerals in throughfall collected in the winter than summer.

Hendry (1977) found higher levels of major ions (including H^+) and N and P forms in throughfall than in bulk precipitation collected during 1976-1977 at a cypress dome north of Gainesville. The higher concentration of H^+ (lower pH) may have been due to leached organic acids, since the TOC levels in throughfall were approximately double those of bulk precipitation. Cronan and Schofield (1979) recently reported higher H^+ levels in throughfall than in bulk precipitation collected on Mount Moosilauke, New Hampshire. The lowered pH corresponded to increased concentrations of organic anions in the throughfall. The throughfall samples collected in this study generally contained visibly colored organic materials; thus some leaching was occurring, but the extent of this, relative to simple washing of accumulated particulates and absorbed gases from the canopy is unknown.

Minor Minerals

1. Silica

Volume-weighted mean silica (SiO_2) concentrations in bulk precipitation (Figure 4-11) ranged from 14 (Lisbon) to 63 $\mu g/l$ (Ft. Myers). Silica levels for most of the sites (coastal, northern and central) were about 20 to 30 $\mu g/l$, and highest values were recorded for three south Florida sites, Fort Myers, Clewiston and Miami. This pattern is similar to that for calcium (Figure 4-9A), and it indicates input of terrigenous substances.

2. Fluoride

Detectable levels of fluoride ($> 20 \mu g/l$) were found in rainfall samples from only 4 sites: Bradenton (28 $\mu g/l$), Lake Placid (29 $\mu g/l$), Lake Alfred (82 $\mu g/l$), and Jasper (55 $\mu g/l$). All four sites are located in or near areas of phosphate mining and processing of phosphate into phosphoric acid for use in fertilizers. This process involves the addition of sulfuric acid to apatite rock ($Ca_{10}(PO_4)_6X_2$; $X = OH$ or F) with the resulting release of fluoride as hydrogen fluoride (HF), some of which escapes into the atmosphere. Tatera (1970) estimated the annual emission of fluoride to the atmosphere at 10^3 tons by this process. No estimates, however, are available for particulate (dust) emissions from the mining and processing of fluorapatite.

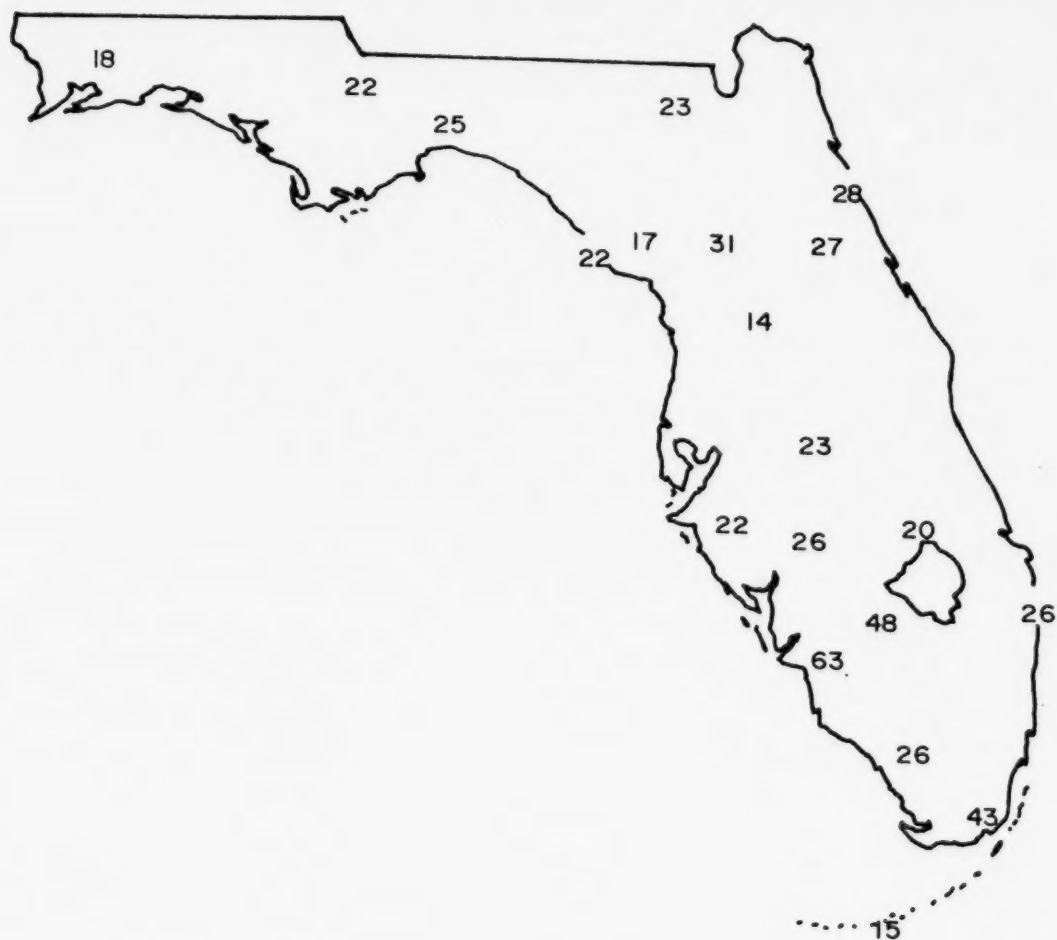


Figure 4-11. Volume-weighted mean concentrations of SiO₂ in bulk precipitation in Florida May 1978 - April 1979. Values in μg/L.

CHAPTER 5. THE ACIDITY OF RAINFALL IN FLORIDA

The atmosphere has long been recognized as an important pathway in the cycling of nutrients and minerals. Numerous recent studies also have shown that many pollutants have significant atmospheric pathways. Acid precipitation is perhaps the most widely known example of this phenomenon, and its occurrence throughout the northeastern United States has been reported extensively (e.g. Cogbill and Likens 1974). The geographic progression of acid rainfall southward and westward has been described elsewhere (Likens 1976; Likens et al. 1979). However, little information is available on the geographic and temporal distribution of acid precipitation in Florida. Two recent studies demonstrated the occurrence of acid rain at Tallahassee (Burton et al. 1978) and Gainesville (Hendry and Brezonik 1980); rainfall at these locations is about 25 to 30% as acidic as the rain in severely affected areas of the Northeast. Nevertheless, data published prior to this study do not delineate the areas of acid precipitation in Florida; nor do they indicate the relative importance of oceanic aerosols and biogenically produced sulfur to Florida rainfall chemistry.

This chapter summarizes results on rainfall acidity (and related parameters) obtained from the statewide precipitation network (FADN) described in Chapter 4. This chapter describes spatial and temporal trends of rainfall acidity in Florida, delineates the southeastern boundary of acid rain in the United States, and discusses the origin and composition of substances affecting the acidity of Florida precipitation.

EXPERIMENTAL METHODS

The sampling network (FADN) of 24 precipitation sites (21 bulk, 4 wet/dry) located primarily at state agricultural and NOAA climatological stations was described in Chapter 4 (see Figure 4-1). Routine chemical analyses relevant to this chapter include major cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+), major anions (Cl^- , SO_4^{2-} , NO_3^-), pH, and specific conductivity. Chemical analyses were done according to accepted methods (see Appendix 1) using standard manuals (APHA (1976) or U.S. EPA (1976)). The pH of rainfall samples was determined as soon as samples were received in the laboratory, using an Orion Model 801 pH meter equipped with a Corning #476002 reference electrode and Corning #476024 pH electrode calibrated at pH 4.00 and 7.00 with Fisher certified buffer solutions. Major anions were analyzed by automated (AutoAnalyzer) procedures: sulfate by the methylthymol blue method, chloride by ferric thiocyanate, and nitrate by the copperized-cadmium wire reduction method. Ammonium ion was measured by an AutoAnalyzer, using the indophenol method; other cations (Na , K , Mg , Ca) were determined by atomic absorption spectrophotometry, using instrument settings and procedures recommended by the manufacturer (Varian 1973).

SPATIAL TRENDS IN ACIDITY AND RELATED PARAMETERS

Average concentrations and depositions of the various acid-mediating species in Florida rainfall are summarized in Table 5-1 for calendar years 1978 and 1979 and the intensive year (May 1978 - April 1979). Tabulated values represent averages for all bulk collectors operative during the period of interest. The following discussion will be limited to the intensive study year (May 1978 - April 1979), during which all 24 monitoring sites were in operation.

Spatial Distribution of Acidity

Results from the sampling network show that precipitation is distinctly acidic over most of Florida (Figure 5-1). With few exceptions, sites north of Lake Okeechobee had annual (volume-weighted) pH values in the range of 4.6 to 4.8, while those south of the lake had acidities approaching geochemical neutrality (i.e. pH 5.6).

Episodes of acid precipitation ($\text{pH} < 5.0$) were observed at all sites except Bahia Honda, McArthur Farms, Clewiston and Fort Myers (Figure 5-1). The first of these sites, far into the Florida Keys, is separated from major point sources of SO_2 and NO_x by at least 50 km and, in spite of seasonally variable local automobile traffic, probably approximates background conditions for the eastern United States.

The high pH values in bulk precipitation at Fort Myers and McArthur Farms probably reflect local effects of cement mining (elevated Ca^{+2} and SO_4^{2-}) and cattle ranching (elevated NH_4^+), respectively. High sodium and calcium concentrations in Clewiston rainfall indicate probable contamination by lakespray from eutrophic Lake Okeechobee ($\text{pH} > 8.0$). These three sites thus show evidence of locally-neutralized rainfall acidity.

Precipitation collected at Lake Placid and Corkscrew Swamp is probably more representative of that occurring over most of South Florida. Both sites are pristine, at least 50 km from point sources of SO_2 and NO_x , and well protected from surface disturbances associated with agriculture and transportation. Bulk precipitation pH values for the study year were 4.95 at Lake Placid and 5.15 at Corkscrew Swamp. In all likelihood, the area receives even higher levels of acidity in rainfall. Based on three months of wet/only rainfall data from Corkscrew Swamp, the volume-weighted mean pH of rainfall probably is less than 5.0 at least this far south in Florida.

Highly acidic events ($\text{pH} < 4.0$) occurred at several northern sites during the study period. The most acidic event ($\text{pH} 3.76$) occurred at Jay in August, 1978. Storms with pH 3.93 were collected at Gainesville in September, 1978 and February, 1979. These events were brief and intense, and because of low rainfall amounts, they correspond to average, or even small H^+ loadings.

In northern Florida, a strong pH gradient is apparent near coastal areas. Bulk precipitation at Cedar Key (on the Gulf Coast, 100 km SE of Gainesville) was only half as acidic as that at Bronson (50 km inland); and rainfall at Marineland (on the Atlantic coast) had less than one-third the

Table 5-1 Summary of concentrations and depositions of H^+ and acid-mediating species in rainfall during various study periods.

Time	Species									
	H^+		NH_4^+		Ca^{2+}		excess- SO_4^{2-}		NO_3^-	
	C*	D**	C	D	C	D	C	D	C	D
Calendar 1978	11.6 (4.94)	161.	15.0	192.	29.6	360	34.2	446.	16.3	209.
Calendar 1979	13.5 (4.87)	215.	10.2	154	31.0	437	27.9	424.	12.6	189.
Calendar 1978-79	12.4 (4.91)	362.	12.4	339.	28.9	759.	30.2	840.	14.1	387.
Intensive year (May 1978 - April 1979)	11.9 (4.92)	170.	12.7	173.	32.6	430.	31.7	433.	14.1	191.

* Concentrations (C) are averages for all operative sites, units are meq/L.

** Depositions (D) are averaged over all sites, units are eq/ha.



Figure 5-1. Volume-weighted mean pH of precipitation throughout Florida, May 1978-April 1979.

acidity of rainfall at Hastings (15 km inland). There are several possible explanations for the coastal neutralization effect: direct titration with marine aerosols, dilution or displacement of polluted air masses by relatively clean maritime air, and enhanced deposition of terrestrially-derived alkaline particles. The first mechanism is of limited significance, as a simple calculation shows. The volume-weighted average concentration of sodium at Marineland was 9.0 mg/L (more than 4x that of any other site). The amount of sea-salt corresponding to this sodium concentration represents about 2.0 $\mu\text{eq/L}$ of oceanic bicarbonate, or only 30% of the observed difference in H^+ concentration between Marineland and Hastings. For the state as a whole the direct input of bicarbonate from seawater to rainfall amounted to less than 0.25 $\mu\text{eq/L}$.

Inspection of Table 5-2 shows that concentrations of excess-sulfate and nitrate were similar at neighboring coastal and inland sites. Coastal rainfall thus is not less acidic than inland rainfall for lack of typically acidic species.

Ammonia and calcium (actually the basic anion associated with Ca) could be responsible for the reduction in precipitation acidity at coastal sites. However, ammonia was present in fairly constant amounts at the two sets of inland-coastal sites in question (Table 5-2), and indeed concentrations of NH_4^+ varied only slightly on a statewide basis (see Chapter 4). Calcium, on the other hand, was present at significantly higher concentrations at coastal sites than at adjacent inland sites. If carbonate were the associated anion, it would have been deposited in sufficient quantities to account for the pH differences between coastal and inland sites.

Thus it appears that a commonly-invoked principle of rainfall neutralization by sea salt is not of great significance for Florida precipitation chemistry. Moreover, daily land-breeze/sea-breeze wind patterns did not significantly alter the deposition of acidic species at coastal locations; similar levels of nitrate and excess-sulfate occurred at the two inland and two coastal sites (Table 5-2). The distinguishing feature of coastal rainfall in north Florida is elevated calcium concentrations, the counterion of which is presumably responsible for high pH values.

The predominant ionic constituents in Florida precipitation vary considerably from location to location; however, the salient geographic trends are clarified when the FADN sites are organized into northern, southern and coastal groups (see Figure 5-2). The northern group of 12 precipitation collectors includes all inland sites north of Bradenton. Rainfall chemistry at these sites was dominated by H^+ and SO_4^{2-} , representing 43% of the cations and 60% of anions, respectively. Compared to the northern sites, precipitation at southern locations (8 inland sites) exhibited a pronounced decrease in acidity, accompanied by a large increase in calcium and the appearance of substantial amounts of bicarbonate. Marine species (Na^+ , Cl^-) contributed significantly to the ionic loading at these sites, indicating the transition from a terrestrial-dominated to a maritime-dominated atmosphere in the southern region of the peninsula. Sulfate levels were about two-thirds as high as in northern precipitation, but levels of nitrate (derived from NO_x emitted somewhat isotropically from mobile sources) and ammonium were similar in the

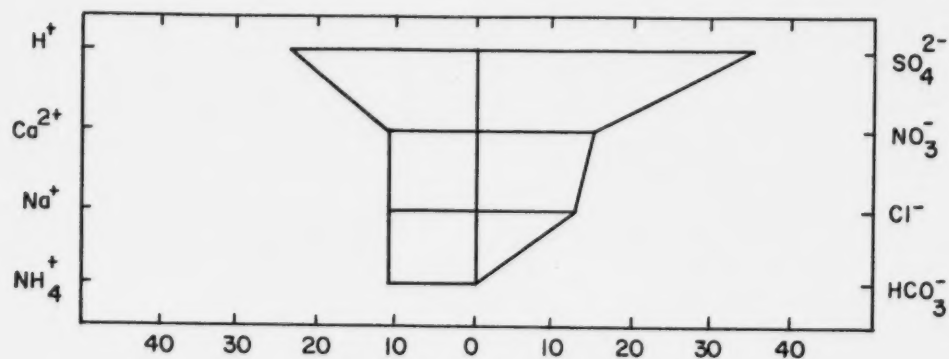
Table 5-2. Comparison of acid-base chemistry of bulk precipitation at two coastal-inland pairs of sites in north Florida.¹

Site	Concentration (µeq/L)				
	H ⁺	NH ₄ ⁺	Ca ⁺²	Excess-SO ₄ ⁼	NO ₃ ⁻
Cedar Key (100 m from Gulf)	9.1	8.2	25.8	24.4	12.1
Bronson (50 km from Gulf)	18.2	10.3	15.8	27.7	10.9
Marineland (100 m from Atlantic)	3.0	7.4	82.0	26.8	17.7
Hastings (25 km from Atlantic)	17.4	7.5	17.0	32.8	11.6

¹. Values are for the year May 1978-April 1979.

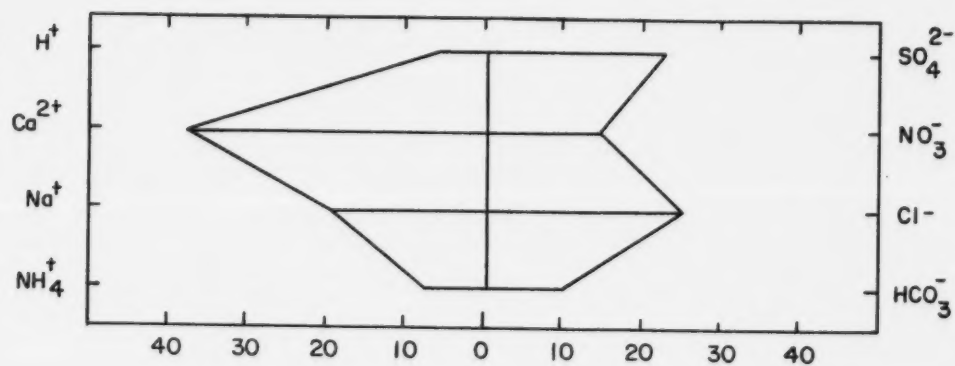
a. NORTHERN

(n=12)



b. SOUTHERN

(n=8)



c. COASTAL

(n=4)

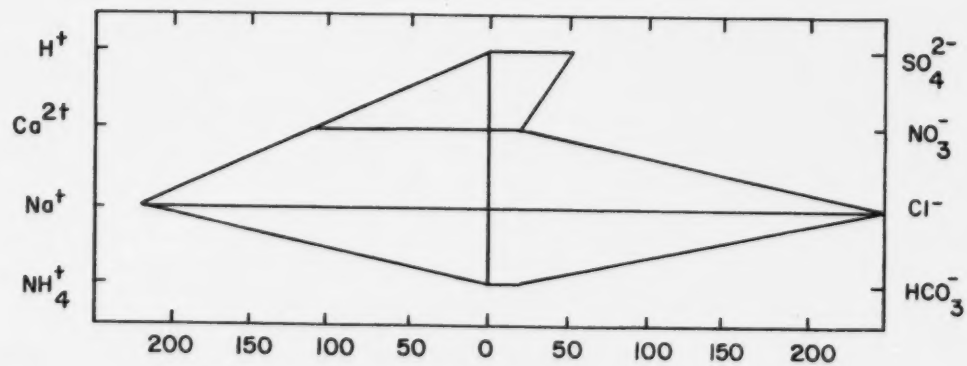


Figure 5-2. Chemistry of precipitation collected at (A) northern, (B) southern and (c) coastal locations. Units are $\mu\text{eq/L}$.

two groups of sites. The north-south differential in SO_4^{2-} concentrations would be larger if the Bradenton site had not been included in the southern group. This site had one of the highest (volume-weighted) mean SO_4^{2-} concentrations in the state (1.88 mg/L) in the intensive year, and it apparently is influenced by large emissions of SO_2 in the Tampa Bay region.

Only at coastal locations (i.e. sites <5 km from the Atlantic Ocean or Gulf of Mexico) did sea-salt constituents dominate the chemical composition of precipitation. Nevertheless, these four sites (two northern: Cedar Key and Marineland, and two southern: Stuart and Bahia Honda) show greater similarity to their inland counterparts than simple ionic balances suggest. Deviation from geochemical neutrality was minimal at these sites, but the cause of this, as previously mentioned, does not appear to involve marine aerosols directly. Significant excess of calcium, sulfate, ammonium and nitrate were found at all sites, after subtraction of the sea-salt component.

Ignoring sea-salt species, southern-coastal precipitation resembles southern-inland precipitation. Northern-coastal rainfall, with the exception of calcium and bicarbonate, likewise is similar to northern-inland rainfall. The exposed soils associated with coastal and southern areas apparently foster entrainment of carbonate species (soil dust, shell fragments, limestone particles) in bulk collectors. Considering wet-only precipitation, there is a high resemblance between northern-inland and northern-coastal precipitation. For example, wet-only samples at Cedar Key were more than twice as acidic as corresponding bulk samples. Similarly, wet-only precipitation collected 100 m from the ocean on Cape Canaveral had a pH of 4.56 (B. Madsen, University of Central Florida, pers. comm., 1979), which is comparable to our value of 4.60 for Orlando, over 50 km inland.

Spatial Trends in Deposition of Acidity.

Deposition of acidity via bulk precipitation during the intensive year (Figure 5-3) ranged from 497 eq/ha at Jay to 21.1 eq/ha at McArthur Farms and averaged 182 eq/ha statewide. The extreme deposition at Jay reflects a combination of intensity and volume factors. Jay had the most acidic bulk precipitation (weighted mean pH 4.62) in the network, as well as the heaviest precipitation (206 cm), during the study year. At McArthur Farms, the situation was completely reversed. Rainfall pH was near geochemical neutrality, and rainfall amount was the lowest in the state. Over the two year period deposition of acidity ranged from 7 eq/ha-yr at Bahia Honda in 1979 to 589 eq/ha-yr at Jay, also in 1979.

For the intensive year, loadings of H^+ at the northern locations ($n=14$) were more than three times those of the southern locations ($n=10$), 272 eq/ha and 82 eq/ha, respectively. This latter value is only 2.6 times greater than would be contributed by geochemically neutral rainfall. In general, loadings mirror the concentration distribution over the state; however, as in the case of the extremes previously discussed, there is some perturbation due to interaction between the concentration field and the rainfall field. This effect will be explored further in a later section.

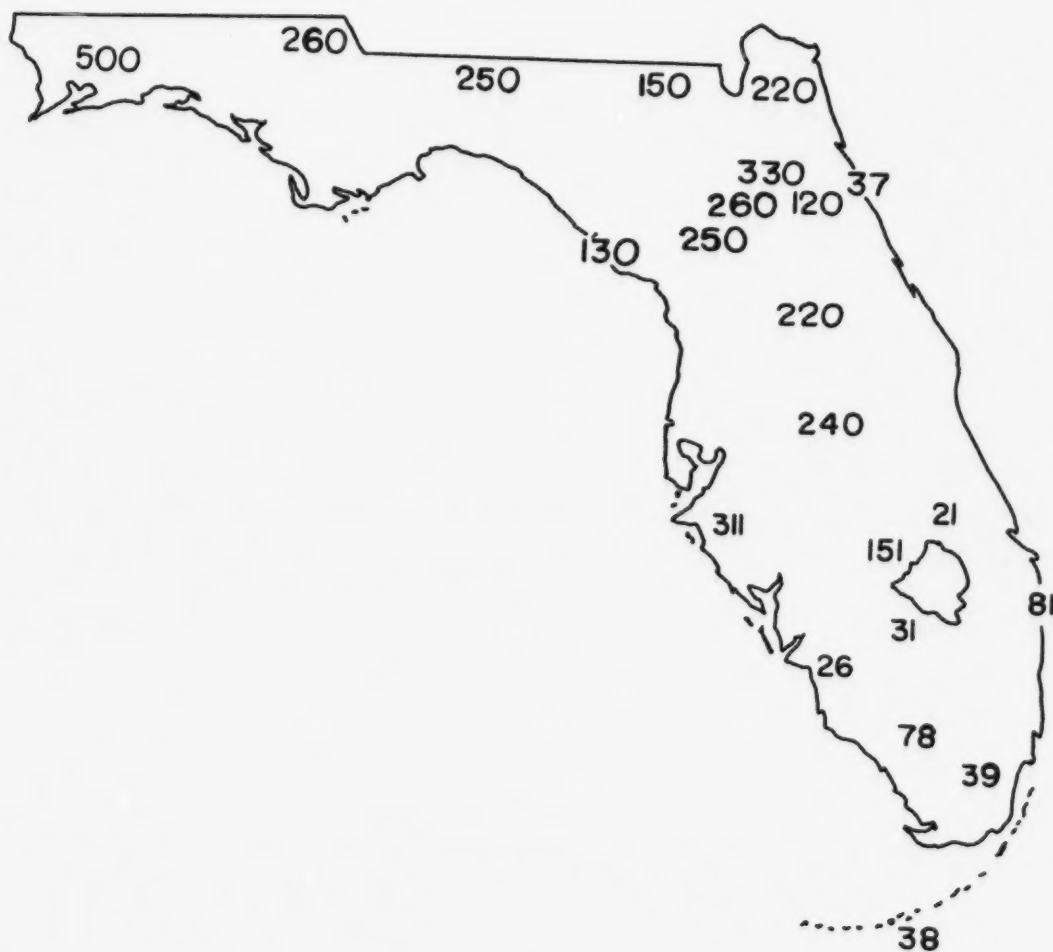


Figure 5-3. Acidity deposition (eq H⁺/ha) throughout Florida for the period May 1978 - April 1979.

Spatial Trends in Sulfate Concentrations.

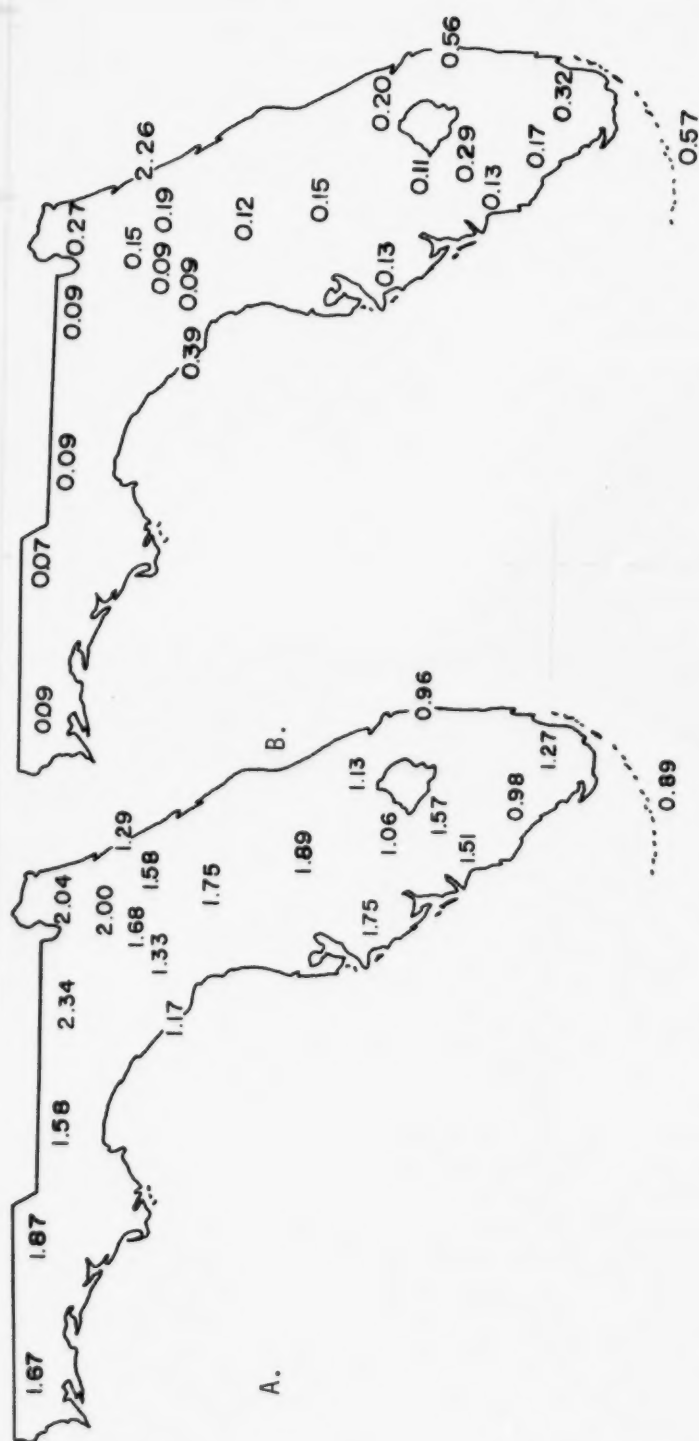
Sulfur occurs in precipitation almost exclusively as sulfate ion (SO_4^{2-}). This fact is attributable to the high levels of sulfate aerosols in the atmosphere relative to other sulfur species, as well as the fact that most forms of sulfur are rapidly oxidized to SO_4^{2-} in aqueous solution. Sulfate in rain can be partitioned into two classes on the basis of origin: sea-sulfate and excess-sulfate. The first of these refers to the sulfate present as a component of sea salt, and is determined from the stoichiometric ratio of sulfate to sodium in seawater: $\text{sea-SO}_4^{2-} = 0.25 \times (\text{Na}^+)$; where all Na^+ in precipitation is assumed to be of oceanic origin. Excess-sulfate is that sulfate having any source other than the ocean (i.e. total-sulfate minus sea-sulfate). On a global scale, the major precursors of excess-sulfate are anthropogenic SO_2 emissions and biogenic emissions, consisting primarily of H_2S , DMS and DMDS. Currently, these two sources of sulfur are thought to contribute about equally to the world sulfur cycle (Granat et al. 1976); however, the former is usually dominant in areas of high population density and industrial activity. The relative importance of these two sources for Florida precipitation will be treated in a later section.

A further distinction between excess-sulfate and sea-sulfate lies in the fact that only excess-sulfate is an acidifying species in precipitation. Numerous rainfall studies (Coghill and Likens 1974; Granat 1972) have shown that excess-sulfate is the dominant mineral acid in acid rain ($\text{pH} < 5.6$). Sea-sulfate, on the other hand, is not associated with H^+ , due to the high pH of the ocean. Based on the ionic composition of seawater, sea-sulfate is predominantly associated with Na^+ and, to a lesser extent, Mg^{2+} . The spatial distributions of excess-sulfate and sea-sulfate in Florida precipitation therefore merit separate discussion.

Concentrations of excess-sulfate in the state varied considerably from north to south (Figure 5-4A). In northern Florida, concentrations ranged from 1.17 mg/L (at Cedar Key) to 2.34 mg/L (at Jasper), and averaged 1.72 mg/L. Over the two year period, Jay had the highest average concentration (2.87 mg/L in 1979), and Bronson had the lowest average concentration (1.14 mg/L also in 1979). Southern values, except for Bradenton (which is affected by Tampa area emissions), were distinctly lower, averaging only 1.14 mg/L in the intensive year. The three most pristine southern sites, Bahia Honda, Corkscrew Swamp, and Stuart, had concentrations of excess-sulfate slightly below 1.0 mg/L. Thus, the concentration of potentially acidifying excess-sulfate varied by a factor of two around the state.

Sea-salt sulfate is a less significant component of Florida rainfall chemistry than might be expected from the peninsular nature of Florida and its extensive coastline. As shown in Figure 5-4b, sea-sulfate concentrations were small everywhere in the state, except for the coastal periphery. Concentrations ranged from 0.09 mg/L, at Tallahassee and Jay, to 2.25 mg/L, at Marineland, and averaged 0.27 mg/L (or 18% of excess-sulfate, statewide).

The average sea-sulfate concentration for the four coastal sites (Marineland, Bahia Honda, Stuart, Cedar Key) was 0.95 mg/L, and only Marineland, had higher sea-sulfate than excess-sulfate. Inland sites, in



contrast, averaged 0.11 mg/L sea sulfate, or only 7% of excess-sulfate concentrations. The rapid disappearance of sea-sulfate with distance from the coast implies that oceanic aerosol particles are relatively large and that the atmospheric lifetime of such aerosols is short, as a result of rapid gravitational settling. The Marineland site had the highest concentrations during both calendar years: 2.12 mg/L in 1978, and 3.25 mg/L in 1979. The higher value for 1979 reflects the influence of hurricane David which passed along the Atlantic coast in September of that year.

Spatial Trends in Sulfur Deposition.

Deposition of sulfate-sulfur in bulk precipitation at the 21 FADN sites during the intensive year ranged from 12.1 kg/ha at Jay to 4.2 kg/ha at Corkscrew Swamp. As in the previous section on concentrations, total-sulfur deposition was divided into its sea-sulfur and excess-sulfur components, and the sites were grouped on the basis of northern, southern, and coastal locations.

Annual deposition of excess-sulfur (Figure 5-5a) thus was high at northern sites (mean = 7.8 kg/ha), intermediate at southern sites (mean = 5.2 kg/ha), and lowest at coastal sites (mean = 4.4 kg/ha). The order is reversed for sea-sulfur (Figure 5-5b), where coastal sites had the highest input, followed by southern, and then northern locations. Excess-sulfur dominates sulfur deposition at all locations except Marineland, where large quantities of sea-salt are deposited near the turbulent coast. The ratio of excess-sulfur deposition at this site was 0.57, whereas inland at Jay the ratio was 18.3. The ratio for the entire state was 5.8.

Annual deposition of excess-sulfur across the extreme northern part of the state (Jacksonville, Jasper, Tallahassee, Chipley, Jay) averaged 9.5 kg/ha, which is similar to the value of about 10 kg/ha reported by Galloway and Whelpdale (1980) for the entire eastern United States. Excess-sulfur deposition is considerably lower only a short distance (~50 km) south, where the average annual deposition for the Cedar Key-Bronson-Hastings-Marineland transect (see Figure 4-1) was 5.8 kg/ha, with a relatively narrow range (5.35-6.41 kg/ha). Still further south, excess-sulfur deposition rose substantially. At the Bradenton, Lisbon and Lake Alfred sites, annual deposition averaged 8.5 kg/ha. This higher rate of sulfur deposition most likely reflects the influence of SO₂ emissions from the Tampa area, where more than 20% of statewide SO₂ emissions originate. The undisturbed sites south of Bradenton (Lake Placid, MacArthur, Stuart, Miami, Bahia Honda) had much lower annual deposition rates of excess sulfur. The average for this group of sites was only 4.1 kg/ha, and values ranged from 3.2 kg/ha at Bahia Honda to 4.8 kg/ha at Lake Placid. Similar geographic trends were observed for both calendar year 1978 and 1979.

Considering the state as a whole, analysis of the various groups of monitoring stations suggests a general trend of decreasing excess-sulfate deposition along the north-south axis. Super-imposed on this pattern is a region, within the central portion of the state, which is influenced by Tampa area emissions.

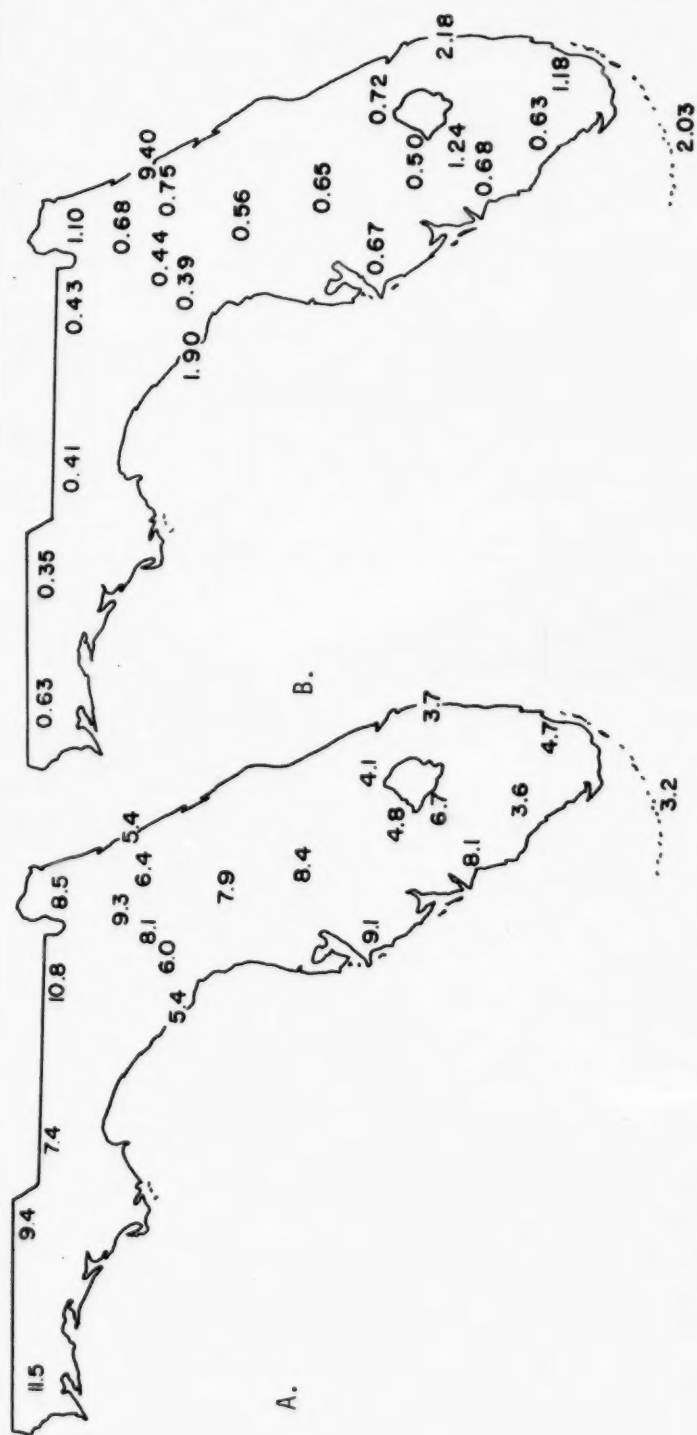


Figure 5-5. Annual deposition (kg/ha) of (A) excess-S and (B) sea-S across Florida.

Acid-Mediating Species in Florida Precipitation.

Ionic balances and Granat-type calculations (Granat 1972) indicate that sulfuric and nitric acids account for the strong acidity of north Florida rainfall. Sulfate contributes about 2.0-2.5 times as much H^+ as nitrate. Chloride is highly associated with sodium and other sea-salt cations and does not influence acidity. Total acidity titrations of Gainesville precipitation (Hendry and Brezonik 1980) demonstrated that samples with ambient pH levels below 5.0 are dominated by strong acid species. The free acidity in such samples averaged about 80% of the total acidity, comparable to values reported for several northeastern locations. As noted by Galloway et al. (1976), weak acids encountered during a titration dissociate well above the initial pH of the rain sample, and thus do not contribute to the observed pH of rainfall.

Regression of H^+ against excess-sulfate for 52 Gainesville wet-only rain samples collected from May 1978 - April 1979 gave a high r^2 (0.70). A similar analysis using volume-weighted annual mean values for all 24 sites resulted in a much lower r^2 (0.25). Multiple regressions of (H^+) versus excess-sulfate and other parameters taken one at a time did not improve the correlation, until Ca^{2+} was added to the expression. Regression of (H^+) against $xs-SO_4^{2-}$ and $xs-Ca^{2+}$ yielded the equation: $(H^+) = 6.1 + 0.54 (SO_4^{2-})_{xs} - 0.35 (Ca^{2+})_{xs}$, $R^2 = 0.75$. Similar results were obtained earlier for Gainesville wet-only precipitation by Hendry and Brezonik (1980). Ammonium and nitrate do not contribute to the explanation of H^+ levels significantly because they are distributed more or less isotropically in precipitation over the state (see Chapter 4). On the other hand, excess-sulfate and calcium (actually H_2SO_4 and $CaCO_3$) vary considerably from site to site statewide; and the degree of neutralization between them determine the pH of Florida precipitation. The endpoint of such an acid-base titration has been attained over most of Florida; i.e. the natural constituents tending to resist change in precipitation acidity appear to have been overcome, especially in the northern part of the state.

The Influence of Rainfall Variability on Network Results.

Up to this point, concentrations and loadings of species have been presented, and geographic trends have been discussed, without reference to the variability of statewide precipitation. Since atmospheric deposition is a function of both concentration and rainfall amount, examination of loading patterns necessarily requires consideration of rainfall patterns, as well. The purpose of this section is to determine the influence of spatially variable rainfall on the chemistry of the precipitation network, and to investigate the manner in which temporally variable rainfall (i.e. deviation from annual norms) affects precipitation chemistry at individual sites.

The first of these topics can be addressed by considering the amount of rain collected at the 24 monitoring stations during the study period. As shown in Figure 5-6a, the 12-month rainfall was uniform over the central portion of the state, relatively high in the Panhandle, and relatively low in the southern area. The average rainfall amounts for the 14 northern and 10 southern sites were 140 cm and 127 cm, respectively. This 9% difference in rainfall between the two groups of sites is small relative to the

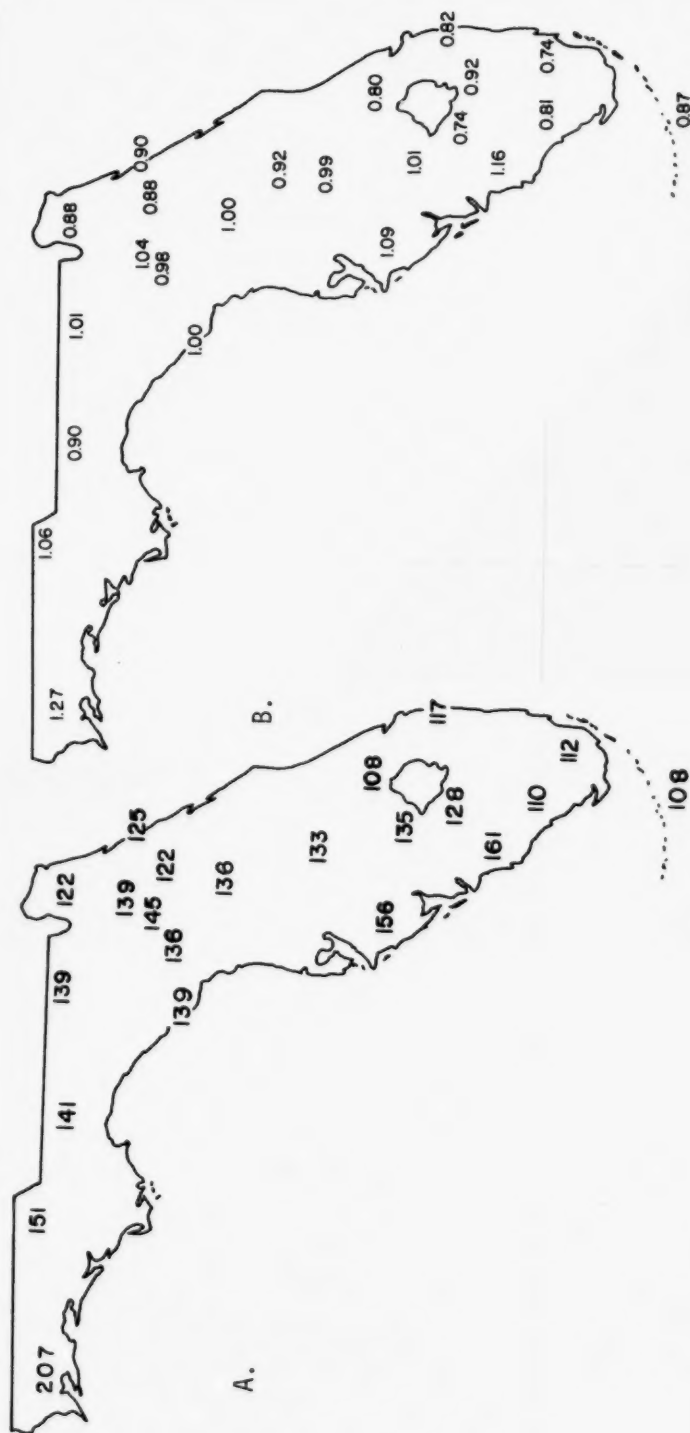


Figure 5-6. A. 12 month rainfall totals (cm) for stations in the Florida Atmospheric Deposition Study, May 1978 - June 1979.
B. Ratio of rainfall totals in (A) to 10-year average (1969-1978) rainfall at identical, or nearby locations.

concentration/deposition differentials observed for many species. Thus, it can be inferred that rainfall amount is not a major factor contributing to the disparate results for northern and southern Florida.

The relationship between statewide deposition values and rainfall amounts was further tested by regression of annual loadings against weighted-mean concentrations and yearly precipitation at all 24 sites. Results of this analysis show that concentration is the dominant variable in the deposition of all major anions and cations (including the various nutrient forms).

The above findings suggest that the regional concentration/deposition pattern is real and not an artifact of rainfall variability; however, there are a number of potential difficulties with the method of spatial averaging. Most important is the possibility that systematic effects are incorporated, rather than eliminated, by such an averaging process. For example, this effect could occur as the result of a significant departure from the average annual rainfall over an entire region (e.g. North Florida vs. South Florida). When only a single year of chemical data is available, this possibility is more serious, because there is no way to smooth results by averaging several yearly values that represent a range in annual precipitation.

Insight into the reasonableness of the data for the individual monitoring sites can be obtained by comparing observed rainfall with long-term annual averages. The ratio of observed-to-average precipitation can be used to infer the true (long term) average concentration and average depositions, assuming that two limiting cases bound the relationship between rainfall chemistry and rainfall amount. In the first case, abnormal rainfall is considered to be a function of the size of the average event. In the second case, high or low annual rainfall can be construed as simply a function of event frequency. For case 1, a wet year would have larger events than usual; hence solute concentrations would tend to be low (compared to the average year). This relationship follows from data for Gainesville, and the concentrations, C , of H^+ , excess- SO_4^{2-} and NO_3^- obey the following expression:

$$C = aR^b$$

where R is the size of an event, and b is in the range -0.55 to -0.65 . However, no relationship has been found between H^+ , SO_4^{2-} , NH_4^+ , NO_3^- concentrations and the period of time between events for Gainesville rain. Rainfall concentrations, then can be taken as invariant with respect to event frequency.

By combining these limiting assumptions, a range of expected concentration/deposition values can be estimated for the individual sites, as a function of annual precipitation. For years with below-average rainfall (i.e. $R/\bar{R} < 1.00$), this yields:

$$1.00 < C/\bar{C} < (R/\bar{R})^{-0.60} \quad (R/\bar{R})^{0.40} > D/\bar{D} > (R/\bar{R}), 1.00$$

where the variables C , R and D represent observed solute concentration, annual rainfall, and deposition, respectively, and overbars denote concentrations and

depositions corresponding to a year with average rainfall (i.e. $\bar{R}$). For years with above average rainfall (i.e. $R/\bar{R} > 1.00$) this yields:

$$(R/\bar{R})^{-0.60} < C/\bar{C} < 1.00; (R/\bar{R})^{1.00} > D/\bar{D} > (R/\bar{R})^{0.40}$$

Referring to Figure 5-6B, it is apparent, on the basis of rainfall amounts alone, that a number of sites may have experienced somewhat unusual rainfall chemistry during the study period. The 1978-79 rainfall at Jay, for example, was 27% higher than the 30-year average for this site, indicating that long-term average concentrations might be higher by as much as 15%, and deposition values lower by 10-20%. For all remaining northern sites, correction factors amount to less than 10%, and so there is little real advantage to their use.

The situation is different for the southern sites, as rainfall was far from average in this part of the state during 1978-1979. Seven of the ten sites received significantly less than average rainfall, while two received somewhat more than average. Clewiston and Miami were the driest sites, with just under 75% of the normal annual rain. For these extreme locations, representative concentration values may be as low as 73% of those reported, while representative deposition values may be 13-35% higher. Correction factors for the other sites are lower than this, but are still significant in most cases.

The mean northern and southern rainfall amounts were 99% and 89%, respectively, of the long-term average. Since the anomalous value for the southern sites raises the possibility that rainfall amount was systematically involved in spatial trends, corrected loadings were calculated for all sites, using excess-sulfate as an example species. Resultant deposition was essentially unchanged for the north Florida group, but deposition may have been up to 13% higher for the south Florida group. Despite these corrections, the excess-sulfate deposition remained statistically higher ($p < 0.05$) in north Florida than in south Florida, even when the upper-limit deposition correction was applied to the latter area.

The findings presented in this section support two conclusions. First, the spatial variation in rainfall during the study year exerted only a minor influence on the overall geographic trends in concentration and deposition. Second, the 1978-79 observations deviate in certain instances from expectations; in a general sense, however, they are representative (especially for northern Florida) of what might be observed during a year of normal (average) precipitation.

Variations in Precipitation Chemistry within the Vicinity of Gainesville.

The statewide precipitation network described above has provided useful information on meso-scale trends in precipitation chemistry, but by itself it does not address the question of local (micro-scale) variability in precipitation chemistry. In addition, the statewide network had no paired stations to compare urban and non-urban rainfall quality for a given area (i.e. a city and its surrounding countryside), although such sites are of interest to obtain information on the geographic extent of urban influence on precipitation chemistry. Consequently, a mini-network of precipitation collectors was

established, and sampled on a weekly basis during the period July-September, 1979. This consisted of a line of three bulk rainfall collectors, spaced at approximately 3 km intervals and extending due south from Gainesville to Paynes Prairie, the dry bed of the former and ephemeral Alachua Lake.

Access to the prairie is controlled by the Florida Department of Natural Resources, and it has no human inhabitants; thus Paynes Prairie is an ideal location for the collection of rural precipitation. The collectors were located at least 2 km from the nearest well-traveled road and from any agricultural activity.

The reference collectors for this study were a wet/dry and a bulk sampler at the University of Florida campus in southwest Gainesville, a semi-urban site with considerable automobile traffic within a few hundred meters in any direction and a small (~50 car) parking lot within 10 m of the collectors. The campus sewage plant is 250 m north of the collectors. The only significant point sources of sulfur oxides in the area are 3 km due east and 15 km northwest of campus. Rainfall sampling at this site was performed on an event basis, as described earlier.

The 10-week volume-weighted mean concentrations of H^+ , NH_4^+ , Ca^{+2} , $SO_4^{=2}$ and NO_3^- for the four sites (Table 5-3) show that the three Paynes Prairie rain collectors yielded similar chemical data. For the rural stations, H^+ exhibited the broadest concentration range (3.9 $\mu eq/L$, corresponding to a pH difference of 0.06 units), but this range is only slightly larger than the inherent uncertainty in pH measurements (~0.03 units) (Galloway and Likens 1979). Concentrations of the remaining major ions were within their respective analytical uncertainties, with the exception of NH_4^+ , which ranged from 3.7 $\mu eq/L$ at site 2 to 6.3 $\mu eq/L$ at site 1. There is no evidence of contamination or of local sources for any of the species analyzed at the Paynes Prairie sites. Rainfall amount was the only parameter exhibiting any trend, (a monotonic decrease with distance from Gainesville), but there was no correlation of the trend with rainfall chemistry.

Comparison of the Paynes Prairie results with those of Gainesville bulk precipitation show that the latter environment appreciably disturbs the bulk deposition of numerous species. This is demonstrated by substantially increased Ca^{2+} and SO_4^{2-} levels, and a reduction of acidity at the Gainesville site. Calcium (actually its counter-ion) is clearly indicated as the neutralizing species of the semi-urban bulk precipitation, i.e. it is the only cation with a sufficient concentration gradient between the Gainesville and Paynes Prairie sites. The correlation of high SO_4^{2-} and Ca^{2+} in Gainesville bulk precipitation suggests that, in the absence of a strong SO_2 or particulate sulfate concentration gradient between Gainesville and Paynes Prairie, the high bulk precipitation $SO_4^{=}$ levels in town may result from scavenging of SO_2 by locally high levels of particulate Ca^{+2} . The nitrogen species NH_4^+ and NO_3^- appear to show slight urban influence, the former ion probably by the nearby sewage treatment plant, and the latter ion perhaps, by automobile traffic in the urban area. However, the magnitude of the differences is small, and their significance is uncertain.

Table 5-3. Comparison of acidic and basic species in Gainesville and Paynes Prairie precipitation, collected 7/12 - 10/1/79. Numbers in parentheses correspond to distances, in kilometers, from Gainesville site.

Location	Rainfall (cm)	pH	Concentration (meq/L)				
			H ⁺	NH ₄ ⁺	Ca ⁺²	SO ₄ ⁼	NO ₃ ⁻
Gainesville wet	41.9	4.49	32.3	6.7	7.3	25.2	14.4
Gainesville bulk	41.9	4.65	22.4	7.1	17.6	32.7	15.6
Paynes Prairie #1 (4)	39.8	4.57	26.8	6.3	5.0	24.8	11.9
Paynes Prairie #2 (7)	38.3	4.57	26.8	3.7	6.1	26.7	13.1
Paynes Prairie #3 (10)	36.8	4.51	30.7	5.4	5.9	25.6	13.9

For the most part, there is a high degree of similarity between the Gainesville wet-only and the Paynes Prairie's bulk precipitation, suggesting that the dryfall component at the rural sites is less significant than that in town. Gainesville wet-only precipitation did have higher concentrations of several species than the Paynes Prairie sites, however (Table 5-3); H^+ was significantly higher at the semi-urban site while Ca^{2+} and NO_3^- were marginally higher. These results underscore the fact that wet collectors also are affected by local perturbations of the environment. Comparing the Gainesville wet-only and bulk results, it is clear that the wet/dry collector is capable of filtering out the greater part of local influence.

Two conclusions can be derived from the mini network. First, the impact of the urban areas on precipitation chemistry is dependent on the type of sampling (wet/dry or bulk) performed. Relative to the University of Florida site, its proximity to Gainesville exerts an important influence on bulk precipitation but only a minor influence on wet-only precipitation. Second, the perturbations of rainfall chemistry caused by Gainesville are of limited spatial extent. At the nearest Paynes Prairie site (4 km from the UF campus), the impact of Gainesville is not discernible from the random variability of the measured parameters. Atmospheric contaminants generated within Gainesville thus blend smoothly into the regional background, either by dispersion or deposition mechanisms, over a scale length of less than 4 km.

WET, BULK, AND DRY DEPOSITION OF ACIDIC AND BASIC SPECIES

Comparison of Wet and Bulk Precipitation Chemistry.

Wet-only precipitation was more acidic than bulk precipitation throughout the state; pH values of wet rainfall were 0.2-0.4 units lower than those of nearby bulk samples (Figure 5-7). These differences may be explained by differences in the relationship between pH and amount of rainfall collected for the two methods of collection. For wet-only samples (Figure 5-8a), (H^+) decayed rapidly with rainfall amount, and leveled off at 10-20 $\mu eq/L$ for large (>2 cm) events. The plot for bulk events differs in that the vertical limb of the previous relationship is absent, and many small storms were almost completely neutralized. Concentrations of H^+ in bulk precipitation tended to increase with amount of rain collected up to about 2 cm of rainfall and then leveled off in the same manner as the wet samples. Apparently, the H^+ content of the initial rainfall (1-2 cm) in bulk precipitation is neutralized by an alkaline component of dryfall, most likely carbonate.

Comparison of wet deposition with bulk (wet plus dry) deposition at five sites (Table 5-4) shows that nitrate, sulfate and ammonium are associated with an acidic wet phase, while calcium is predominantly a component of dry deposition. The anion associated with calcium thus neutralizes rainfall in bulk collectors and is responsible for differences observed between neighboring wet and bulk samplers (Figure 5-7). At Gainesville, the average precipitation event (2.50 cm of rain) deposited 600 and 450 $\mu eq H^+/m^2$ in wet and bulk collectors, respectively. The difference is almost exactly balanced by the 147 $\mu eq/m^2$ of bicarbonate deposited (on the basis of cation excess) in statewide dryfall samples between collections.



Figure 5-7. Comparison of annual weighted mean pH of bulk (above slash) and wet-only (below slash) precipitation. Locations are, from north to south: Gainesville, Cedar Key, Apopka, Belle Glade.

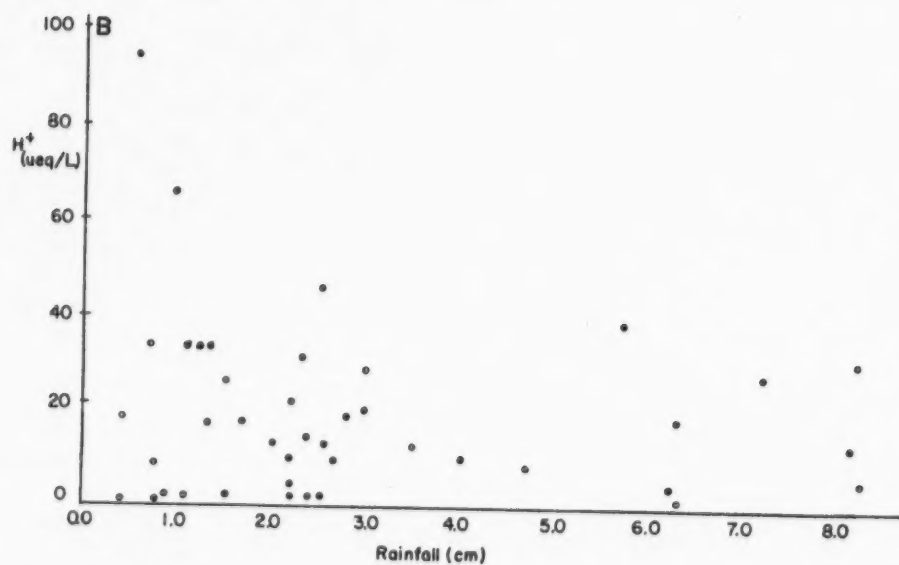
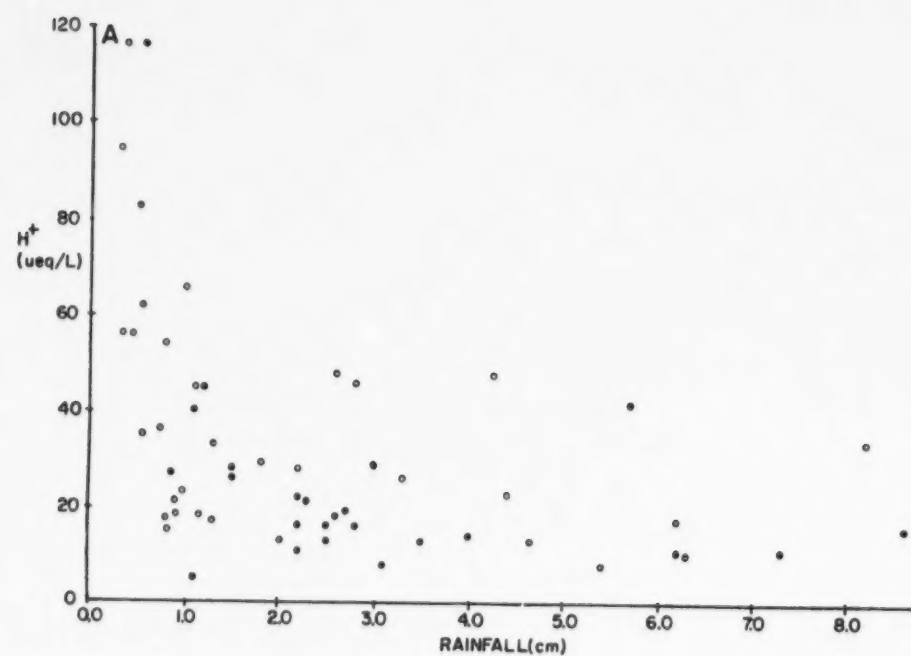


Figure 5-8. Relationship of H^+ concentration to rainfall amount for winter (●) and summer (○) wet-only events (A) and bulk events (B) collected at Gainesville.

Table 5-4. Relative loadings in wet versus total (wet + dry) precipitation. Values correspond to % deposition from wet-only precipitation.

Location	H ⁺	Na ⁺	K ⁺	Ca ⁺²	Mg ⁺²	NH ₄ ⁺ -N	NO ₃ ⁻ -N	Excess SO ₄ ⁼	Cl ⁻
Gainesville (semi-urban)	100	59	59	31	40	88	68	74	61
Apopka (Agricultural)	100	57	55	52	45	73	74	77	61
Belle Glade (Agricultural)	100	59	60	40	45	85	72	75	60
Cedar Key (Gulf Coast)	100	81	72	54	69	82	62	88	81
Cape Canaveral* (Atlantic Coast)	100	18	18	24	19	71	61	71	17

*B.Madsen, University of Central Florida, Orlando, personal communication, 1979.

Dry Deposition of Acidic and Basic Species.

Dry deposition is widely recognized as an important mechanism of nutrient and mineral input to ecosystems (see Chapter 4). Dry deposition involves a variety of interaction mechanisms between surfaces of variable resistance to deposition, aerosols over a broad size range, and gases of widely disparate reactivities, and it involves two distinct physical processes: eddy and gravitational deposition. The first of these relates to transport of gases and sub-micron particles to receptor surfaces via turbulent eddies. Gravitational deposition is simply the settling of relatively large particles ($> 2 \mu\text{m}$) due to gravitational forces that impart high settling velocities to these particles.

The purpose of this section is twofold: 1) to examine the significance of dry deposition versus wet deposition for species related to acid precipitation, and 2) to determine the influence of season on dry deposition rates.

The relative importance of wet and dry deposition for species that affect rainfall acidity is summarized in Table 5-4. Hydrogen ion, excess- SO_4^{2-} , NO_3^- and NH_4^+ are highly associated with an acidic wet phase. Being gases or sub-micron aerosols, these species have insignificant settling velocities and small dry deposition rates. The nature of the collector buckets also may affect dry deposition of these species; this topic is addressed later. The terrigenous species Ca^{2+} is deposited primarily through dryfall. Apparently Ca^{2+} occurs in the atmosphere in supra-micron particles that have significant settling velocities. Furthermore, the dryfall bucket is near ($\sim 1 \text{ m}$) to the source of calcium (i.e. the soil), and it probably is influenced by steep concentration gradients near the surface.

Annual loading rates of alkalinity, excess- SO_4^{2-} , NO_3^- , Ca^{2+} , NH_4^+ to dryfall collectors at five locations within the state are summarized in Table 5-5. Alkalinity was inferred by ionic balance and presumably reflects carbonate. This represents an appreciable fraction of the total dryfall loading at all sites. Dry deposition rates of Ca^{2+} and alkalinity follow the pattern Belle Glade $>$ Gainesville $>$ Cedar Key $\approx$ Apopka. Agricultural activity (sugarcane, winter vegetables) in the Belle Glade area results in the injection of large quantities of particulates (e.g. dust, soil particles) into the atmosphere. The Apopka area, though agricultural, is planted largely to citrus, which requires substantially less tillage than do the crops grown at Belle Glade. Dry deposition of excess- SO_4^{2-} followed a similar but less pronounced trend, but the inorganic nitrogen species showed very different trends both from each other and from the three other acid-related species.

Dry deposition rates for the major inorganic species were generally higher during winter than summer (Table 5-6). The striking exception to this is NH_4^+ , two-thirds of which was deposited during summer. This trend reflects enhanced evolution of NH_3 from soils during the warm months. The seasonally disparate deposition rates at Belle Glade are the result of local agricultural practices (burning of sugarcane fields during winter and early spring, with resulting large emissions of particulate matter to the atmosphere). Deposition of soil-derived species is enhanced directly by this process. Crop burning has been shown to release most of the sulfur contained in vegetative

Table 5-5. Annual dry deposition of acid-mediating species at four Florida sites.

Location	Alkalinity*	equivalents/hectare			
		Ca^{2+}	NH_4^+	xs-SO_4^{2-}	NO_3^-
Gainesville	173	315	19.3	159	57.1
Apopka	105	152	29.1	104	49.2
Cedar Key	90	182	18.5	84.2	72.3
Belle Glade	741	868	21.2	153	87.2

* Alkalinity inferred from net excess of analyzed anions. Value for Belle Glade is probably a several-fold over-estimate, due to high deposition of soil organic matter (associated with Ca^{2+}) at this site.

Results are for the year May 1978 - April 1979.

Table 5-6. Comparison of winter (Nov-Apr) and summer (May-Oct) dry deposition of major ionic species.¹

Location	Seasonal deposition (kg/ha)						
	Na ⁺	K ⁺	Ca ⁺²	Mg ⁺²	NH ₄ ⁺ -N	NO ₃ ⁻ -N	SO ₄ ⁼ Cl ⁻
Gainesville							
Winter	1.35	0.27	3.46	0.36	0.09	0.42	3.82 2.53
Summer	0.95	0.27	2.84	0.46	0.18	0.38	3.82 2.01
Apopka							
Winter	1.83	0.64	1.97	0.35	0.21	0.36	2.84 2.91
Summer	1.67	0.53	1.06	0.25	0.19	0.33	2.14 2.64
Cedar Key							
Winter	2.84	0.29	2.04	0.46	0.09	0.53	2.18 5.02
Summer	1.79	0.27	1.59	0.29	0.16	0.48	1.83 3.26
Belle Glade							
Winter	2.80	1.15	9.70	0.91	0.08	0.60	4.68 5.90
Summer	1.65	0.71	7.65	0.49	0.22	0.62	2.67 3.57

¹Results are for the period May 1978-April 1979.

tissue (J. Ewel, Univ. Fla. pers. comm. 1979), and deposition of SO_4^{2-} may be enhanced by this practice, first by the release of SO_2 and second by the attachment of SO_2 to combustion-generated particulates.

High wintertime deposition rates for Ca^{+2} at other sites may be the result of seasonally high winds. A similar seasonal trend in sea-salt species (see Table 4-9) apparently reflects enhanced atmospheric injection, as well as rapid transport inland by strong winter winds. Soil species such as Ca^{+2} also should have augmented suspension and deposition rates due to seasonally high surface turbulence.

Seasonal differences in precipitation frequency also may influence the seasonal pattern of dry deposition. All other factors being equal, the more often the atmosphere is cleansed by rain, the lower the time-averaged concentration of contaminants. Precipitation events in Florida occur approximately once a week during winter, and two to three times a week during summer. Therefore the levels of various pollutants, particularly those preferentially scavenged by washout processes (eg. Ca^{+2}), should be lower during the summer. Insufficient seasonal data on concentrations of mineral constituents in the atmosphere are available to test the validity of this concept.

TEMPORAL PATTERNS IN PRECIPITATION ACIDITY

Seasonal Trends.

Summer rains (May-Oct) are more acidic (by 0.2-0.3 pH units) than winter rains (Nov-Apr) throughout the state (Figure 5-9). In summer, the pH 4.7 isopleth encompasses all of the panhandle and about half of the peninsular portion of the state, and there is no geochemically neutral rain ($\text{pH} > 5.6$) anywhere in the state. During the winter, the pH 4.7 isopleth is displaced to the north of the state and is replaced by a pH 5.0 contour. Geochemically neutral rain occurs in large areas of the southern peninsula during this season.

The seasonal and spatial dichotomies of Florida precipitation are underscored in Figure 5-10, which illustrates monthly volume-weighted mean concentrations of H^+ , excess SO_4^{2-} , and NO_3^- for the northern ($n=14$) and southern ($n=10$) sites during the 1978-79 one-year period. As previously stated, H^+ was higher in northern sites than southern sites, and was highest in the north during the summer months. Southern precipitation varied less in H^+ concentration from month to month, but H^+ was clearly higher in the summer than in the winter.

In the north, excess SO_4^{2-} and NO_3^- exhibited similar seasonal patterns. Excess SO_4^{2-} levels were consistently high during summer (May-Oct) and low during winter (Nov-Apr). The lowest SO_4^{2-} concentrations occurred, as with H^+ , during the relatively dry months of transition between convective and frontal storm activity (November, December and April). Nitrate concentrations generally adhered to the above pattern, but during the dry months of November and April, levels of NO_3^- were elevated rather than reduced. The contrasting behavior of excess- SO_4^{2-} and NO_3^- during these two months reflects the fact

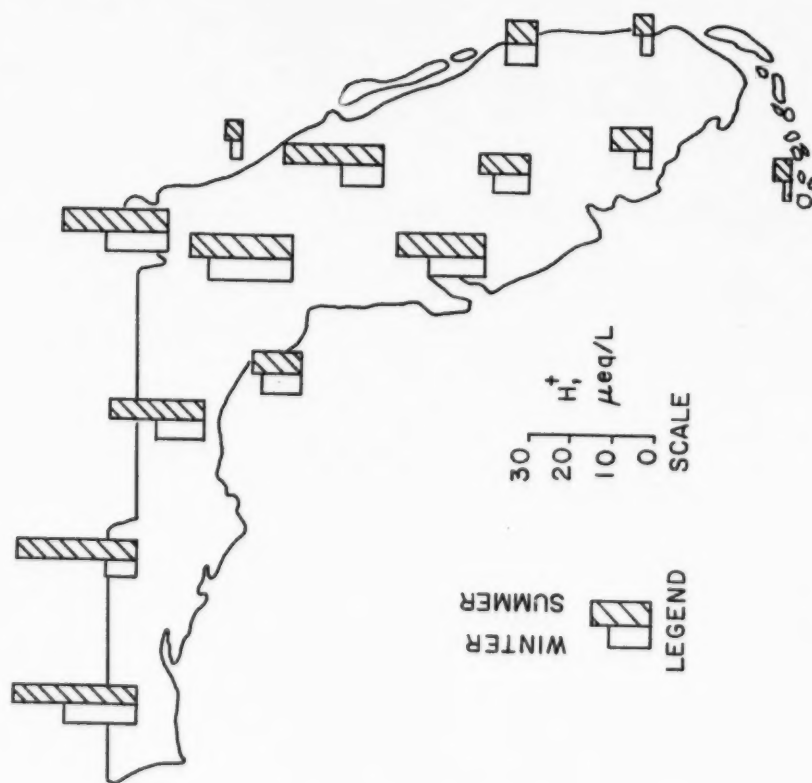


Figure 5-9. Volume-weighted mean H^+ concentration for summer (May-Oct) and winter (Nov-Apr) across Florida. For clarity, not all sites are depicted; statewide means (all sites) are shown in legend.

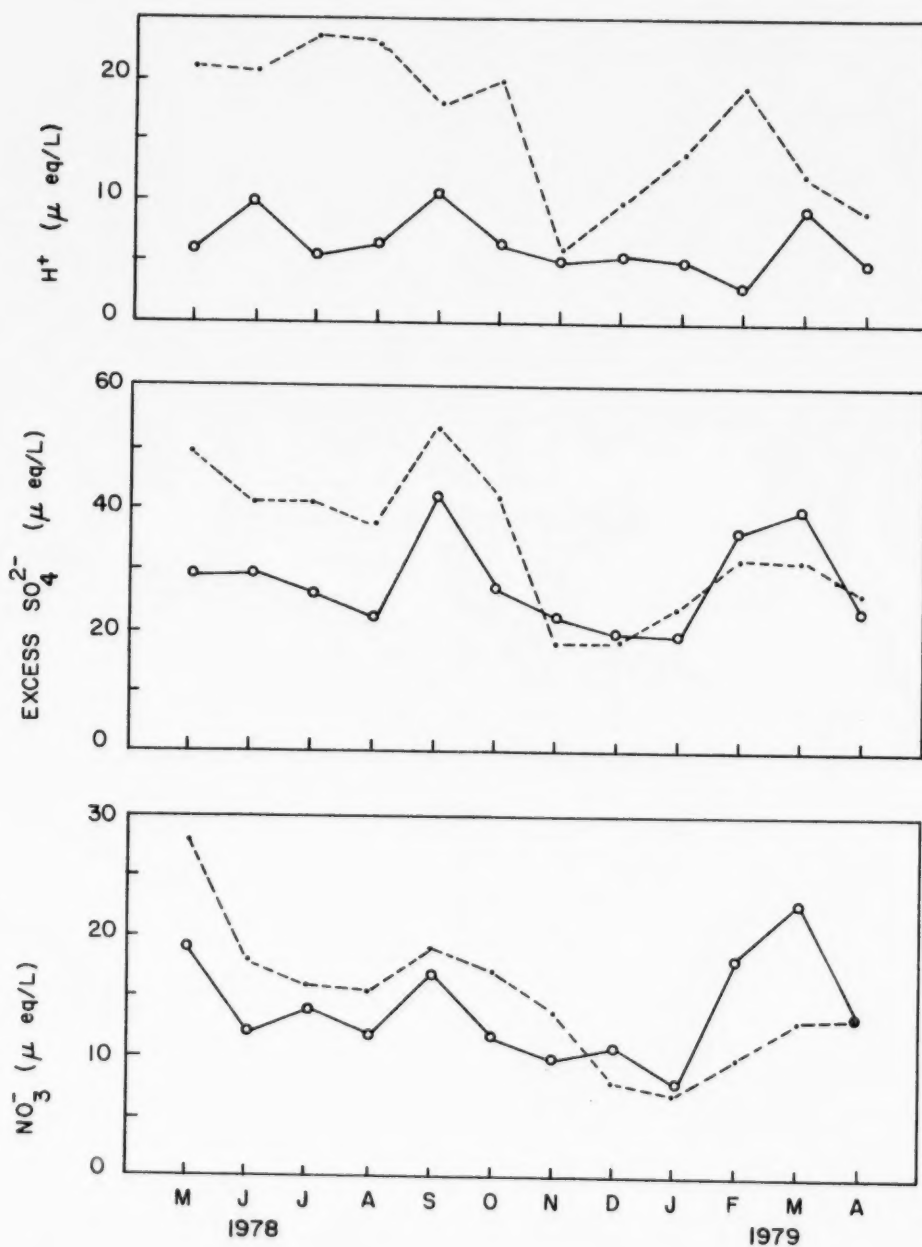


Figure 5-10. Monthly volume-weighted mean concentrations of H^+ , excess- SO_4^{2-} and NO_3^- for 14 northern (----) and 10 southern (o---o) locations.

that dryfall represents a greater proportion of NO_3^- deposition (33%) than of excess SO_4^{2-} deposition (24%).

There was no clearly defined seasonality in concentrations of excess SO_4^{2-} and NO_3^- in south Florida precipitation. The transition months exhibited the lowest values, but the average winter concentration did not differ significantly from the average summer concentrations. Both anions were as high (or higher) in southern-winter precipitation as in northern-winter precipitation, a reversal of the summertime relationship between the two groups of sites. Frontal precipitation occurs in Florida approximately once a week during winter, and these widespread systems of rainfall probably confer a degree of homogeneity to wintertime precipitation chemistry. Additionally, southern areas receive less rainfall than northern areas during winter (because the cold fronts weaken as they progress southward).

Despite the seasonal concentration variations described above, the deposition of H^+ , excess- SO_4^{2-} and NO_3^- was considerably higher at both northern and southern locations during summer than winter (Table 5-7). Wintertime depositions in the north were 29-34% of the annual total, even though winter rains accounted for 43% of the yearly rainfall. In south Florida, winter deposition of H^+ , excess- SO_4^{2-} and NO_3^- were 25-32% of the annual total; these values are similar to the seasonal rainfall disparity (winter rainfall was 28% of annual total).

Sequential Sampling within Rainfall Events.

In order to elucidate the infrastructure of winter and summer events, several frontal and convective storms were sampled sequentially within the events. A funnel on the roof of Black hall was uncovered and rinsed immediately prior to the onset of rainfall. Subsamples (25 mL), corresponding to 0.05 cm of precipitation, were collected for the first 1.0 cm of each event; thereafter 50 mL samples were taken until cessation of rainfall. Each fraction was analyzed for H^+ , Na^+ , K^+ , Mg^{+2} , Ca^{+2} , NH_4^+ , $\text{SO}_4^{=}$, NO_3^- , Cl^- and conductivity.

Results of the chemical analyses indicate that temporal features of both convective and frontal events can be complex. H^+ concentration, for example, did not always decrease during an event, as might be expected from the classical "washout curve" exhibited in Figure 5-8a. Rather, H^+ and other ions (generalized in the figure by conductivity) were observed to increase, decrease or oscillate rapidly within rapidly within events (Figure 5-11). No clear-cut differences between frontal and convective storm types are evident, based on the sampling performed to date.

During most of the events, the major ions (H^+ , NH_4^+ , Na^+ , Ca^{+2} , $\text{SO}_4^{=}$, NO_3^- , Cl^-) generally behaved coherently, e.g. concentrations rose and fell in harmony with variations in conductivity. Regression analysis, however, showed that correlations among certain ions consistently were good, while others were poor. Na^+ , excess $\text{SO}_4^{=}$, NO_3^- and NH_4^+ , for example, correlated well with H^+ ; the soil-derived elements (Ca^{+2} , Mg^{+2} , K^+), on the other hand, correlated poorly with H^+ . These findings indicate that different processes (i.e. rain-out and washout) may affect those species associated with H^+ and those not

Table 5-7. Seasonal deposition of acidic and basic species in bulk precipitation at northern, southern and coastal Florida locations. ¹

Location	Season	Rainfall (cm)	Deposition (eq/ha)				
			H ⁺	NH ₄ ⁺	Ca ⁺²	Excess-SO ₄ ⁼	NO ₃ ⁻
Northern (n = 12)	Winter	59.9	81	58	161	162	62
	Summer	80.0	187	139	159	361	153
	Annual	140	269	197	320	523	215
Southern (n = 8)	Winter	37.8	17	33	192	88	443
	Summer	88.7	67	105	280	253	133
	Annual	126	84	138	472	341	176
Coastal (n = 4)	Winter	51.5	30	26	281	113	64
	Summer	84.1	40	87	300	198	108
	Annual	136	70	113	581	311	172

¹. Results are for the periods May-October 1978 (summer) and November 1978-April 1979 (winter).

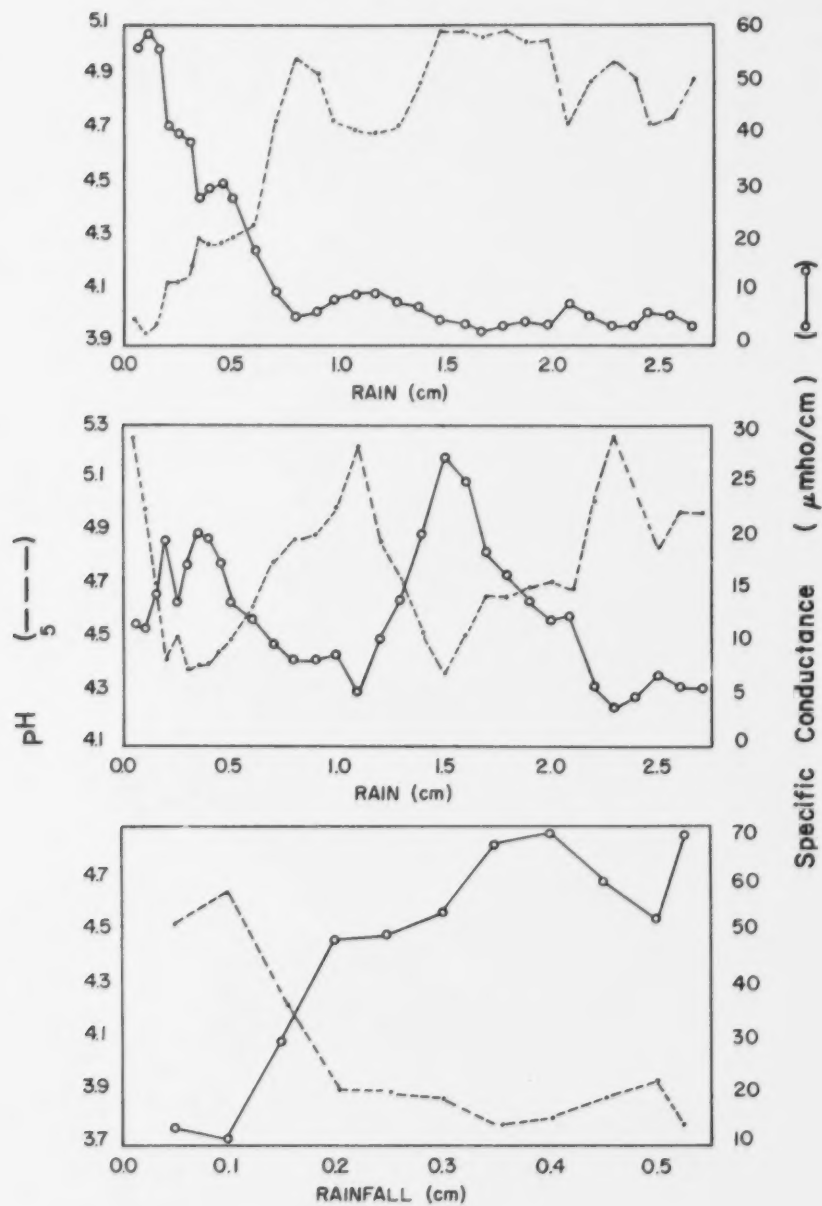


Figure 5-11. Temporal variation of pH and conductivity within 3 events sequentially sampled at Gainesville.

associated with H^+ during an event. For example, Ca^{2+} is derived from terrigenous particles with large mass-median diameters and thus is rapidly scavenged by below-cloud processes (washout). Particulate sulfate, on the other hand, occupies a range of very small particle sizes (Ahlberg et al. 1978) and is poorly removed via washout.

The above findings may present a clue to the origin of acidic species in winter (frontal) precipitation. Frontal events that occur in Florida during winter are generated by the collision of a cold dense air mass of arctic origin with a warm, humid air mass of maritime provenance. In the process, the warmer, unstable air is uplifted, causing condensation of moisture and precipitation (Byers 1974). Due to the different source regions of the two air masses, only the uplifted (maritime) air has a significant burden of sea-salt species (e.g. Na^+ and Cl^-), and thus these are deposited in frontal precipitation by the process of rainout. Based on the correlation of sea-salt and acidic species, deposition of the latter forms probably follows the same mechanism. The bulk of the H^+ , excess SO_4^{2-} and NO_3^- in frontal precipitation thus may originate in the southern air, rather than the northern, or mid-western, air; the acid species and their precursors thus appear to be primarily of local origin. Of course, this scheme is an oversimplification because there is mixing between northern and southern air masses when they come into contact. The degree of mixing is of interest in determining the proportion of local vs. imported pollutants in Florida wintertime precipitation.

SOURCES OF ATMOSPHERIC SULFUR IN FLORIDA

Estimates of the global significance of biogenic sulfur emissions are numerous and controversial (Eriksson 1960; Kellogg et al. 1972; Friend 1974; Granat et al. 1976). Florida has extensive areas of potential importance for biogenic sulfur emissions, and consequently it seems appropriate to attempt an assessment of the contribution of anthropogenic and biogenic sulfur in the Florida atmosphere. Approximately 20% of the state (3×10^6 ha) is occupied by wetlands: fresh and salt water marshes and swamps and poorly-drained soils (Smith et al. 1973; Coultas 1976; Coultas and Gross 1972; Coultas 1978). The most productive of these areas (tidal flats and mangrove swamps) occur predominantly in southern coastal areas where conditions of available organic carbon and sea-sulfate, coupled with high year-round temperatures, could give rise to considerable biological sulfate reduction.

Published experimental data on emissions from such areas are scarce, in general, and non-existent for Florida. Emission estimates are further complicated by the fact that a wide variety of experimental designs has been employed in reported studies. Nevertheless, the available data have been synthesized (Table 5-8) to give a general overview of the potential emissions of biogenic sulfur in Florida, and the results indicate a range of annual biogenic sulfur emissions of about 770 to 51,800 metric tons, (or 0.05-3.34 kg S/ha) statewide. These figures could be higher if temperature differentials, or other factors, enhance the rates of biogenic sulfur emission in Florida. On the other hand, if slowly-oxidized organic sulfur species (e.g. COS, CS₂) were the predominant emissions from wetland areas, most of this sulfur would be exported from the state before it could be oxidized to SO₂.

Table 5-8. Inventory of Florida wetlands and potential biogenic sulfur emissions.

Wetlands	Area ¹ (m ²)	Potential Emission ² Rate (mg-S/m ² -yr)	Total Emission (Tons-S/yr)
Freshwater Swamps, Marshes	1.2 x 10 ¹⁰	< 10 - 100	120 - 1200
Poorly-drained Organic Soils	1.6 x 10 ¹⁰	< 10 - 100	160 - 1600
Tidal Mudflats	3.0 x 10 ⁹	< 10 ² - 10 ⁴	300 - 30,000
Mangrove Swamps	1.9 x 10 ⁹	< 10 ² - 10 ⁴	<u>190 - 19,000</u>
		Total	770 - 52,000

¹ Sources: Smith et al. 1973; Coultas 1976, 1978; Coultas and Gross 1972.

² Hitchcock 1975; Maroulis and Bandy 1976; Jaeschke 1978; Adams et al. 1979; Aneja et al. 1979; Aneja and Aneja 1979.

Another means of generating biogenic emission figures involves the use of areal emission rates developed by various authors to balance global sulfur budgets. These "calculated" emission factors range from about 0.53 kg S/ha-yr (Granat et al. 1976) to about 3.8 S/ha-yr (Friend 1973). Multiplying these factors by the area of the state yields annual emissions of 8,200-60,000 metric tons-S, which agrees fairly well with the previous reckoning.

The above figures are small compared to anthropogenic sulfur within Florida. Statewide sulfur emissions for 1975 were 500,000 metric tons (32.3 kg S/ha). The geographic distribution of these emissions was very uneven; 85% of total emissions occurred in the northern 58% of the state, and county-wide average emissions ranged from 1.2 to 428 kg S/ha-yr (Figure 5-12).

In comparison, wet and bulk sulfur deposition values for 1979-79 were 83,000 and 100,000 metric tons, respectively. Estimated biogenic emissions amount to no more than 72% and 55% of wet and bulk deposition (and perhaps much less). Moreover, the geographic distribution of biogenic emission shows little correspondence with the observed pattern of excess sulfate deposition. Consequently, biogenic sulfur probably plays only a small role in Florida precipitation chemistry. Anthropogenic emissions, on the other hand, are more than six times wet deposition and five times bulk deposition, and distribution of high emissions correlates roughly with the area of high rainfall deposition of excess-sulfate.

This is not to say that biogenic sulfur is not a constituent of Florida precipitation; however, it is not likely to be the dominant sulfur species in precipitation anywhere in the state. We also do not imply that sources of sulfur outside the state do not contribute to sulfur loadings within Florida. Nonetheless, there are several reasons to suspect that such emissions are of limited importance. First, emissions of SO_2 within Florida are substantial and amount to roughly 40% of emissions in Ohio, which ranks first nationally (U.S. EPA 1976). Second, during summer Florida is isolated meteorologically from large northern SO_2 sources by the prevailing synoptic weather patterns (southerly air flow). This period corresponds to one of heavy deposition of excess sulfate and enhanced precipitation acidity throughout the state (see Figure 5-9 and Table 5-7). Unless a mechanism exists for significant diffusion counter to the direction of advective transport, there is little reason to believe that much of the sulfur in summertime precipitation originates in the Midwest. Lastly, as mentioned in the sequential sampling section, there is some evidence that much of the sulfur in winter (frontal) precipitation is also of local origin. Consequently, out-of-state sources probably account for only a small fraction of the annual sulfur deposition in Florida.

ACID RAINFALL IN FLORIDA: A PERSPECTIVE

Historical Trends in Florida Precipitation Chemistry

The historical record of precipitation chemistry in Florida unfortunately is incomplete, and there is no exact way to establish the date when acid rain first appeared in the state. However, two rainfall studies conducted in the

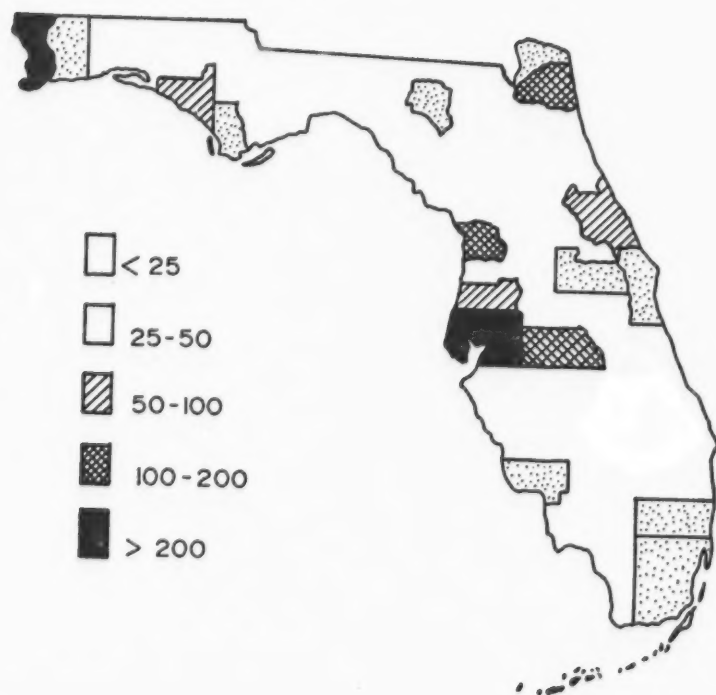


Figure 5-12. County-wide emissions of SO_2 across Florida for 1978. Units are kg-S/ha-yr. Statewide mean is 32 kg-S/ha-yr; mean of underlined county emissions in 6.2 kg-S/ha-yr.

mid-1950s do yield some insight concerning man's alteration of precipitation during the past quarter century.

Junge's well-known study of U.S. precipitation (Junge and Werby 1958) included five sites that are comparable to FADN sites. Although pH was not measured in the former study, the chemical analyses were complete enough to estimate H^+ concentrations via ionic balances. Comparison of annual volume-weighted mean concentrations of hydrogen ion, excess SO_4^{2-} and NO_3^- for 1955-56 and 1978-79 (Table 5-9) indicate that the levels of these species at each site have increased markedly over the 24-year period. A deficiency of measured anionic equivalents compared to measured cationic equivalents was found for each of Junge's Florida sites, suggesting that bicarbonate (an unmeasured species) was present in the rainfall of that period. Consequently, although exact pH values cannot be computed from Junge's data, the results indicate that Florida rainfall was at or above geochemical neutrality ($pH > 5.6$; $H^+ < 2.5 \mu eq/L$). The average increment of excess sulfate plus nitrate ($23.5 \mu eq/L$) over the period is sufficient to account for the average increase in hydrogen ion ($\sim 15 \mu eq/L$). It should be noted that this analysis compares wet-only data (Junge's) with bulk precipitation data (ours). Because concentrations in bulk precipitation are somewhat different than those in wet-only precipitation (cf. Figures 5-8), this leads to a magnification of the current excess of sulfate and nitrate compared to the levels found in 1955-56. In contrast, the 24-year increment of H^+ is underestimated, since wet precipitation typically is more acidic than bulk precipitation.

The other historical study, conducted by the USDA (Jourdan et al. 1959) to evaluate atmospheric inputs of sulfur to southeastern soils, also had five sites comparable to present ones. Annual loadings (kg/ha) of sulfate-sulfur in bulk precipitation (Figure 5-13) increased at all five sites between 1952-55 and the present. Atmospheric loadings in the northern part of the state have increased by 3-4 fold, while deposition in southern Florida has increased marginally, and perhaps not significantly. Assuming that sea-sulfur and biogenic sulfur emissions have remained relatively constant over the period, anthropogenic sulfur emissions are the cause of the increased deposition at northern sites.

Wet-only precipitation events have been collected for over three years in Gainesville. Monthly weighted mean pH values for the period January 1977 - December 1979 (Figure 5-14) fail to indicate any recent trend in precipitation acidity. Annual weighted mean pH values of precipitation for 1977, 1978 and 1979 are 4.51, 4.62 and 4.56, respectively. The uniformity of these results suggests that the current data base can function as a barometer for gauging future changes in precipitation chemistry.

Comparison of Florida and Northeastern Precipitation

Comparison of precipitation loadings of H^+ and related parameters for Florida and Hubbard Brook, New Hampshire show that the acid rain phenomenon is considerably more intense in the Northeast. Two factors are responsible for this difference. First, the levels of acidifying substances (excess-sulfate and nitrate) are somewhat lower in Florida rain. At northern, southern and coastal sites in Florida (Figure 5-2), the sum of these anions is 43, 38 and

Table 5-9. Comparison of parameters related to the acidity of Florida rainfall in 1955-56 and 1978-79.

Location	Weighted-Mean Concentration ($\mu\text{eq/L}$)					
	H^+		excess-SO_4^{2-}		NO_3^-	
	1956*	1978-9	1956*	1978-9	1956*	1978-9
Mobile/Jay	2.5	24.0	16.0	34.7	2.6	13.9
Tallahassee	2.5	17.4	18.8	33.0	2.9	13.9
Jacksonville	2.5	18.3	27.9	43.5	2.9	16.2
Tampa/Bradenton	2.5	20.1	28.8	36.4	2.7	14.3
W. Palm Bch./Stuart	2.5	6.9	13.5	20.1	4.1	12.1
Mean	2.5	17.3	21.0	33.5	3.1	14.1
1978-9/1956	> 8.4		1.6†		4.5†	

* Proton concentration inferred via anion/cation balance; data from Junge (1958) and Junge and Werby (1958).

† Present data are for bulk precipitation (rainfall collectors open at all times), whereas 1956 data are for rainfall-only (collectors open to atmosphere only during rain events). Adjacent wet-only (W) and bulk(B) collectors at Gainesville in the study have yielded the following volume-weighted concentrations (in $\mu\text{eq/l}$): excess sulfate, 35.1 (B) and 26.6 (W), B/W = 1.3; nitrate, 16.9 (B) and 13.6 (W), B/W = 1.24. Thus differences in collector type do not wholly explain the increases in concentrations. Time period for present data: May 1978-April 1979.

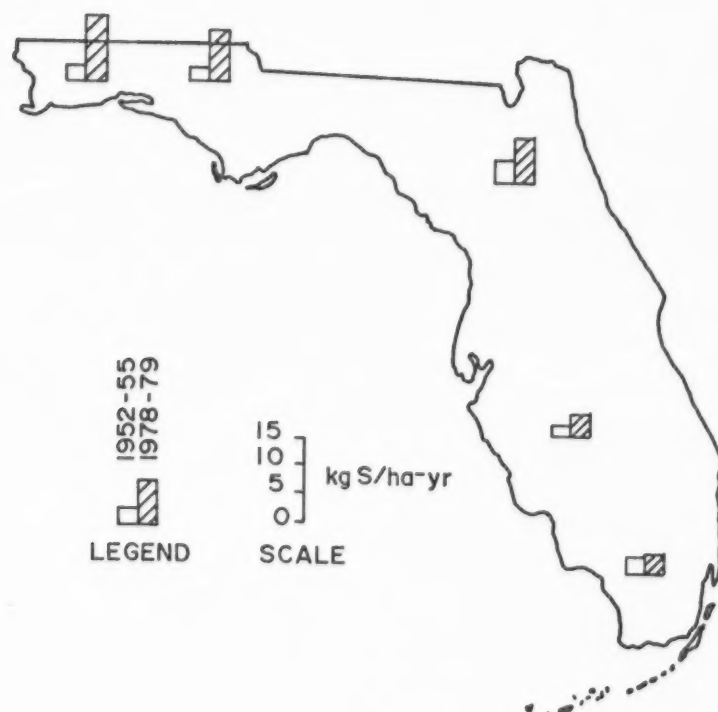


Figure 5-13. Atmospheric sulfur deposition at 5 historical (1952-55) and current (1978-79) precipitation sampling locations. Means for both studies are depicted in legend.

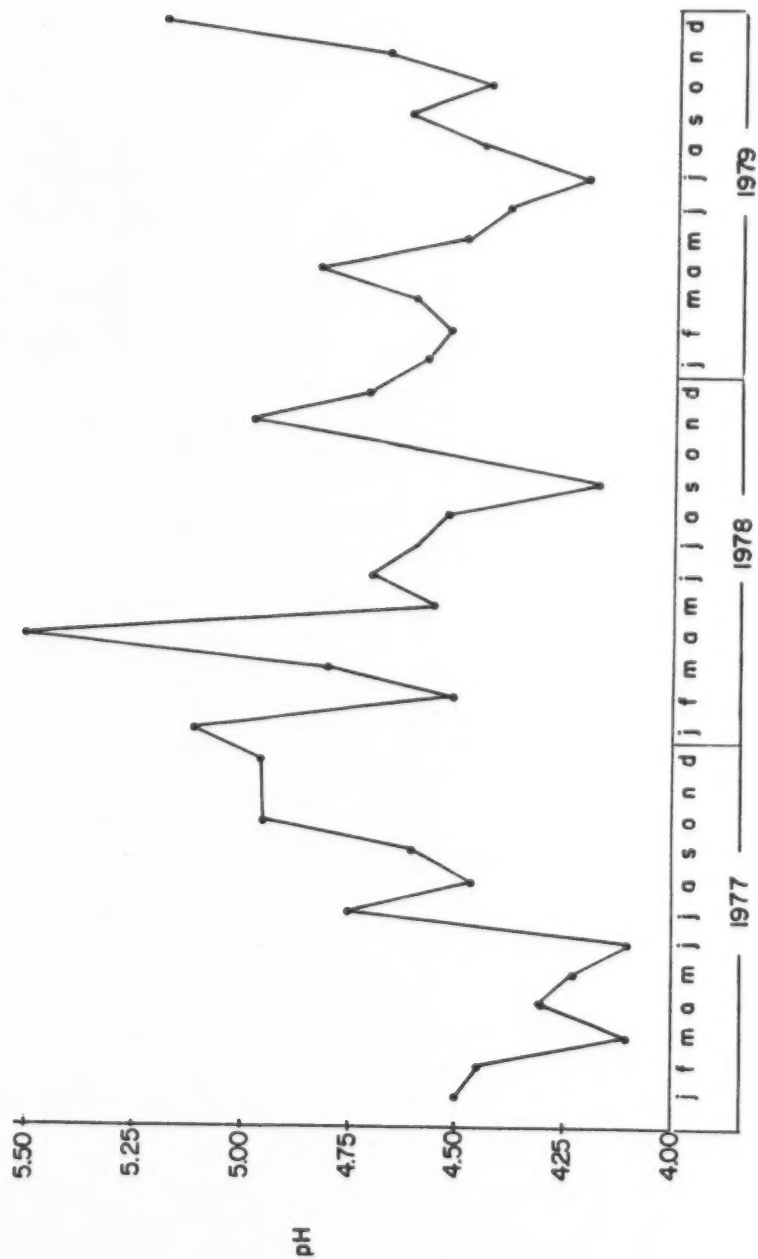


Figure 5-14. Monthly weighted mean pH of Gainesville wet-only precipitation collected from January 1977 to December 1979.

43%, respectively of the 10-year average for these anions at Hubbard Brook, NH (Likens et al. 1977). Second, calcium (and presumably carbonate) occurs at much higher concentrations (3-4 fold) in Florida rainfall.

The effect of these two circumstances is especially apparent at the coastal and southern Florida sites. The rain at these sites typically is only slightly acidic compared to geologically neutral rain. Were it not for the excess of calcium in Florida rain compared to levels in rainfall of the northeastern United States, all of Florida would now be receiving acid precipitation: northern areas would have a pH of about 4.5, and southern sites would exhibit pH levels of about 4.7.

Because Florida generally receives more rainfall than the Northeast, annual deposition of acidity and related species is closer to northeastern values than concentration data alone suggest. For the state of Florida as a whole, bulk deposition of H^+ averaged 175, 200, and 190 eq/ha for 1978, 1979, and the intensive year, respectively. Corresponding statewide averages for bulk deposition of excess sulfate are 7.4, 6.8, 7.2 kgS/ha. As noted above, deposition of both H^+ and excess sulfate was higher throughout the northern part of the state. For example, the site at Jay received slightly over 200 cm of rainfall during the intensive year (an unusually wet one), resulting in the deposition of 500 eq H^+ /ha and 11.5 kg S/ha. Corresponding values at Lake Apopka, where the rainfall amount was near normal for the state, are: 136 cm, 342 eq H^+ /ha, and 6.6 kg S/ha. At Hubbard Brook, deposition averaged 970 μ eq H^+ /ha (Likens 1976) and 12.7 kg S/ha (Likens et al. 1977) in the 10-year period 1964-65 to 1973-74. Thus northern Florida receives about one-third to one half of the H^+ deposition and 50 to 90% of the sulfate deposition as that in the most impacted region of the United States.

CHAPTER 6. EFFECTS OF ACIDIFICATION ON SOFTWATER LAKES IN FLORIDA

A total of 20 lakes in two geographical regions were selected for sampling during 1978-79, for a variety of physical, chemical and biological parameters. The sampling was designed to evaluate chemical and ecological impacts of acidic precipitation on sensitive aquatic systems. The lakes were selected on the basis of two main criteria: 1) softwater, making the lakes susceptible to acidification, and 2) availability of historical data to determine whether there have been any measurable changes (i.e. decreases in lakewater pH and alkalinity) over the last decade or so.

This chapter describes the sampling program conducted on these lakes, temporal trends in chemical composition of the lakes over the past 20 years, and the variations in composition of the major biotic groups in the lakes as a function of pH.

PREVIOUS STUDIES ON EFFECTS OF ACID PRECIPITATION ON AQUATIC ECOSYSTEMS

Acid rain in North America and Europe has contributed to the acidification of many aquatic habitats, with subsequent effects on the biota (Gorham 1976; Hornbeck et al. 1976; Oden 1976; Overrein 1976; Schofield 1976; and Likens et al. 1979). With increased acidity, effects have been documented for all trophic levels and include reduced species richness, deformities, reproductive failures, retarded growth rates and deteriorated health. In some severe cases the complete loss of an entire class of organisms can be traced to increases in acidity (Beamish 1976; Stokes and Hutchinson 1976 and Andersson et al. 1978).

Much valuable information on the effects of increased acidity on aquatic systems has been obtained from studies of acid mine drainage (e.g. Harp and Campbell 1967; Parsons 1968, 1976). Although the rate of acidification by mine drainage is often more rapid than by acid rain, the general responses by the biota are often similar.

The impact of acidification on lakes in Norway has led to the development of a comprehensive project by the Norwegian Research Council (Braekke 1976) designed to investigate the effects of air pollutants on soil, vegetation, water, and freshwater fish (Overrein 1976). Literature reviews on the responses of aquatic organisms to increased acidity are presented in EIFAC (1969), Giddings and Galloway (1976), and Wright (1976).

Parsons (1976) proposed that three major parameters be investigated in assessing the impact of increased acidity on an ecosystem: 1) quantitative analysis of populations, 2) community structure and 3) the ability of the various species to establish a complete life cycle.

Phytoplankton

Effects of increased acidity on phytoplankton communities include reductions in species richness and alterations in the proportions of the species

present (Leivestad et al. 1976). As species richness decreases, species normally found in low abundance may disappear, while acid-tolerant species such as Euglena sp. increase in dominance. In a study of growth rates of 34 species of freshwater algae, Moss (1973) found Euglena gracilis and Eunotia sp. to be very acid-tolerant and to survive at pH 3.65 and 3.9 respectively. Leivestad et al. (1976) reported that periphytic algae become dominant in acid streams. In their study, the periphytic diatom Tabellaria flocculosa and the green alga Mougeotia sp. accounted for 70% or more of the total number of algae cells in a stream acidified to pH 4.0 - 4.3. Very few periphytic algae were found in streams at pH 6.0. The high abundance of periphytic algae in the acidic stream, resulted in a higher algal biomass at pH 4 than pH 6.

The effects of increased acidity on phytoplankton communities can be caused by direct physiological damage or by synergistic interactions between acidity and toxic substances such as heavy metals (Stokes and Hutchinson 1976). Giddings and Galloway (1976) suggested that increased free CO₂ concentrations in acidic lakes could favor some species while inhibiting others.

Changes in pH have been shown to affect interspecific competition in phytoplankton. For example, Kroes (1971) found that the inhibitory effect of Chlorococcum ellipsoidum on Chlamydomonas globosa was the result of a change in pH brought about by C. ellipsoidum.

Macrophytes

Macrophyte communities in temperate lakes have been shown to be greatly reduced in species richness by acid precipitation (Hultberg 1976). In a study by Grahn (1976), the natural vegetation of an oligotrophic lake in Sweden was reduced from Lobelia dortmanna, Littorella uniflora and Isoetes lacustris to a monoculture of Sphagnum spp.

Productivity

Acid precipitation is thought to decrease the overall productivity of a body of water (Grahn 1976). This process is known as oligotrophication and involves a decrease in available plant nutrients caused by chemical and biological changes in acidified systems (Overrein 1976). Planktonic productivity is reduced by large mats of Sphagnum because of their ability to concentrate cations and their formation of a physical barrier between the sediment and the water column (Grahn 1976). Another aspect of oligotrophication involves a reduction in the rate of biological decomposition of organic matter. Andersson et al. (1978) showed a replacement of bacteria by fungi as the major agents of biologic decomposition in acid waters. This replacement results in decreased nutrient cycling and thus lower productivity.

Zooplankton

Zooplankton communities have been shown to be adversely affected by acid precipitation, with decreases in species diversity and abundance of individuals occurring in acidified lakes (Hagen and Langeland 1973; Hendrey et al. 1976). Sprules (1975) reported that pH has a major effect on the structure of zooplankton communities. The greatest effect was noted in lakes of pH 5.0 or

less, where many species were completely eliminated. Some acid-tolerant species were found by Sprules to occur throughout the pH range (3.8 - 7.0) of his group of lakes, including Mesocyclops edax, Cyclops bicuspidatus, Diaptomus minutus, Holopedium gibberum and Bosmina sp. Species absent from lakes of pH 5 or less were Tropocyclops prasinus, Diaptomus oregonensis, Leptodora kindtii and several species of Daphnia.

When determining acid tolerance for a particular species, both the pH level for survival of adults and the pH at which reproduction stops must be considered. Davis and Osburn (1969) conducted tolerance studies on Daphnia pulex and found a survival time of at least 32 hours over a wide range of pH (4.3 - 10.4). However, the organisms reproduced successfully only within the pH range 7.0 - 8.7. Consequently, Daphnia is not commonly found in acid waters. Yan (1979) found the small cladoceran Bosmina longirostris comprised 89% of all adult crustacea in a group of acidified Canadian lakes. Because of the reduced biomass (resulting in part from the small size of the dominant species), Yan proposed that zooplankton exert less control over phytoplankton communities in acid-stressed lakes than in neutral lakes.

The ability of some zooplankton species to adapt to acidic conditions was demonstrated by Parsons (1968). In his study, acid and non-acid waters were found to contain some of the same species. When individuals from a species common to both types of water were removed from nonacidic water and subjected to acidic conditions, a high rate of mortality was observed.

Benthic Invertebrates

Benthic invertebrate populations have lower species richness and reduced numbers of individuals in acidic waters (Tomkiewicz and Dunson 1976). Harp and Campbell (1967) found that Chironomus plumosus was the only chironomid established in water of pH 6.0 or below. The presence of C. plumosus was also highly correlated with the presence of leaf litter and sediment type.

Gastropods are sensitive to low pH, as demonstrated in a study by Økland (1969) in which snails were absent from Norwegian lakes with a pH below 5.2. Benthic crustaceans such as amphipods are an important food source for many fish, and they are adversely affected by high acidity (Hutchinson and Havas 1979). Avoidance of acidic conditions by Gammarus pulex was shown by Costa (1967). G. pulex showed negative responses to pH levels of 5.4 or less, with graded avoidance between 5.6 and 6.4. Bell (1971) found caddis flies to be most acid-tolerant with mean 30-day survival limits of pH 2.45 to 3.38 and a 50% failure of emergence at pH 5.9.

Fish

Loss of commercial and sport fishing from many lakes in Scandinavia has been reported (Wright and Snekvik 1978). Similar losses have been reported in the northeastern United States and Canada (Parsons 1968; Beamish and Harvey 1972; Schofield 1976). Fish losses from acidic waters can be traced to a number of factors, such as increased toxicity of heavy metals, ionic imbalances, and especially increased concentrations of aluminum in acidic waters (Schofield 1979; Packer and Dunson 1970).

In studies by Leivestad et al. (1976) and Wright and Snekvik (1978), reproductive failures were noted prior to the loss of fish populations from some acidic lakes. Beamish (1974, 1976) found abnormally low levels of serum calcium in the ovaries of female trout exposed to low pH levels. Females with low calcium levels failed to release their ova for fertilization and reabsorbed much of the ovarian tissue back into their bodies (Beamish 1974).

Acid precipitation can contain high concentrations of heavy metals and increase leaching of cations from soils (Beamish and Harvey 1972; Schofield 1976; Cronan and Schofield 1979; Malmer 1976). Among the metals associated with acid precipitation, aluminum has been shown to exert detrimental effects on organisms at high concentrations ($>150\text{--}200\text{ }\mu\text{g/L}$) (Dickson 1978). Dickson (1978) suggested that unsuccessful attempts to restock some Swedish lakes with rainbow trout after the pH had been increased by liming may be due to aluminum toxicity. However, aluminum is insoluble at neutral pH, and it should precipitate in limed lakes.

DESCRIPTION OF THE STUDY REGIONS AND LAKES

Two groups of soft-water lakes were chosen for study of the effects of precipitation on lake chemistry and biology; a northern group of 13 lakes in the Alachua, Clay, and Putnam Counties and a group of 7 lakes in Highlands County in south-central Florida. Figure 6-1 shows the location of the two lake groups, and table 6-1 lists each lake, its surface area, elevation, and county location.

Topography

The two lake districts are topographically similar. Each group is located along a ridge (the Trail Ridge (north) and Highlands Ridge (south)) within the topographic division of the state known as the Central Highlands (Clark et al. 1962). The Trail Ridge extends southward along the Bradford-Clay County line as a series of hills, with the highest elevation being 75 m (250 ft) above MSL just south of Kingsley Lake. From this point, the land slopes in a southerly direction and fans out into a wider area of sand hills dotted with lakes. The Highland Ridge is a narrow, elongated area of rolling uplands containing numerous hills and lakes, extending from northwestern Highland County, southwestward almost to the Glades-Highlands County line, and ranges in elevation from about 60 m (200 ft) to 12 m (40 ft) above MSL.

Geology

The two regions are geologically similar (Figure 6-2), being underlain by several hundred feet of unconsolidated to semiconsolidated marine and non-marine deposits of sand, clay, marl, gravel, limestone, dolomite, and dolomitic limestone. The oldest formation penetrated by water wells in both areas is the Lake City limestone of Eocene Age (Clark et al. 1964; Bishop 1956). The Eocene series is comprised, in addition to the Lake City limestone, of the Avon Park and Ocala Group limestones, which collectively are referred to as the Floridan Aquifer, and are the major source of fresh water supplies in the state. The top of the uppermost limestone layer, is approximately 30 m (100

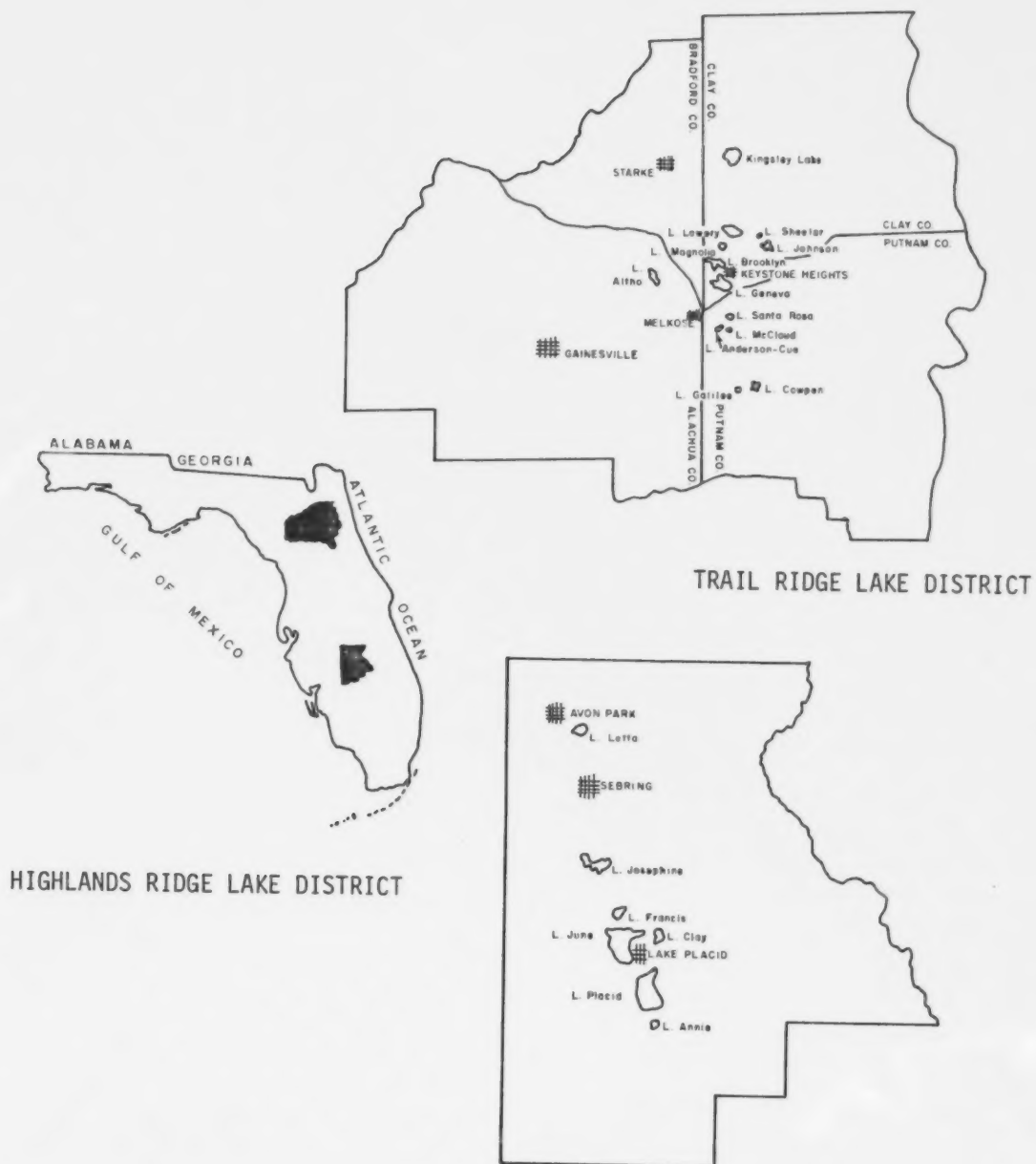


FIGURE 6-1. Location of the lakes in the survey.

Table 6-1. Locations and Physical Data on Lakes in Survey.

Lake	Surface Area (ha)	Mean Depth (m)	Maximum Depth (m)	Elevation (m above MSL)	Location (County)	Previous Studies (Ref. no)
<u>Trail Ridge Group</u>						
1 Altho	216	3.6	5.8	45	Alachua	2,6
2 Anderson - Cue	8	2.0	4.6	38	Putnam	5,6
4 Brooklyn	256	5.7	10.4	35	Clay	1,3,6
6 Cowpen	223	3.7	8.8	21	Putnam	6
8 Galilee	34	3.5	5.8	27	Putnam	6
9 Geneva	650	4.1	8.8	32	Clay	1,3,6
10 Johnson	140		4.0	27	Putnam	1
13 Kingsley	652	7.3	26.0	54	Clay	1,3,6
15 Lowery (Sand Hill)	500	4.8	12.0	40	Clay	1,4,6
16 Magnolia	83	8.0	15.0	38	Clay	1,6
17 McCloud	10	2.0	5.0	27	Putnam	5,6
19 Santa Rosa	42	8.1	13.4	30	Putnam	6
20 Sheeler	7		17.0	49	Clay	
<u>Highlands Ridge Group</u>						
3 Annie	35	8.3	20.0	34	Highlands	7
5 Clay	147	4.0	8.0	24	Highlands	
7 Francis	216	2.9	8.0	21	Highlands	2
12 June (Stearns)	1403	6.0	12.0	22	Highlands	3,7
11 Josephine	494	2.0	3.0	22	Highlands	7
14 Letta	191		3.0	30	Highlands	3
18 Placid (Childs)	1329	8.0	17.0	28	Highlands	7
1) Clark et al. (1964). Semi-annual sampling 1957-60. 2) Hennessey and Holcomb (1967); Holcomb (1968), (1969); Duchrow (1970,71,72); Holcomb and Starling (1973). Annual sampling 1966-73. 3) Holcomb (1968,69); Duchrow (1970,71,72); Holcomb and Starling (1973). Annual Sampling 1967-72. 4) Duchrow (1970,71,72); Holcomb and Starling (1973). Annual Sampling 1969-72. 5) Brezonik et al. (1969). Biweekly and monthly sampling 1967-68. 6) Shannon (1970). Quarterly sampling 1969. 7) Milleson (1978). Quarterly sampling 1974-76.						

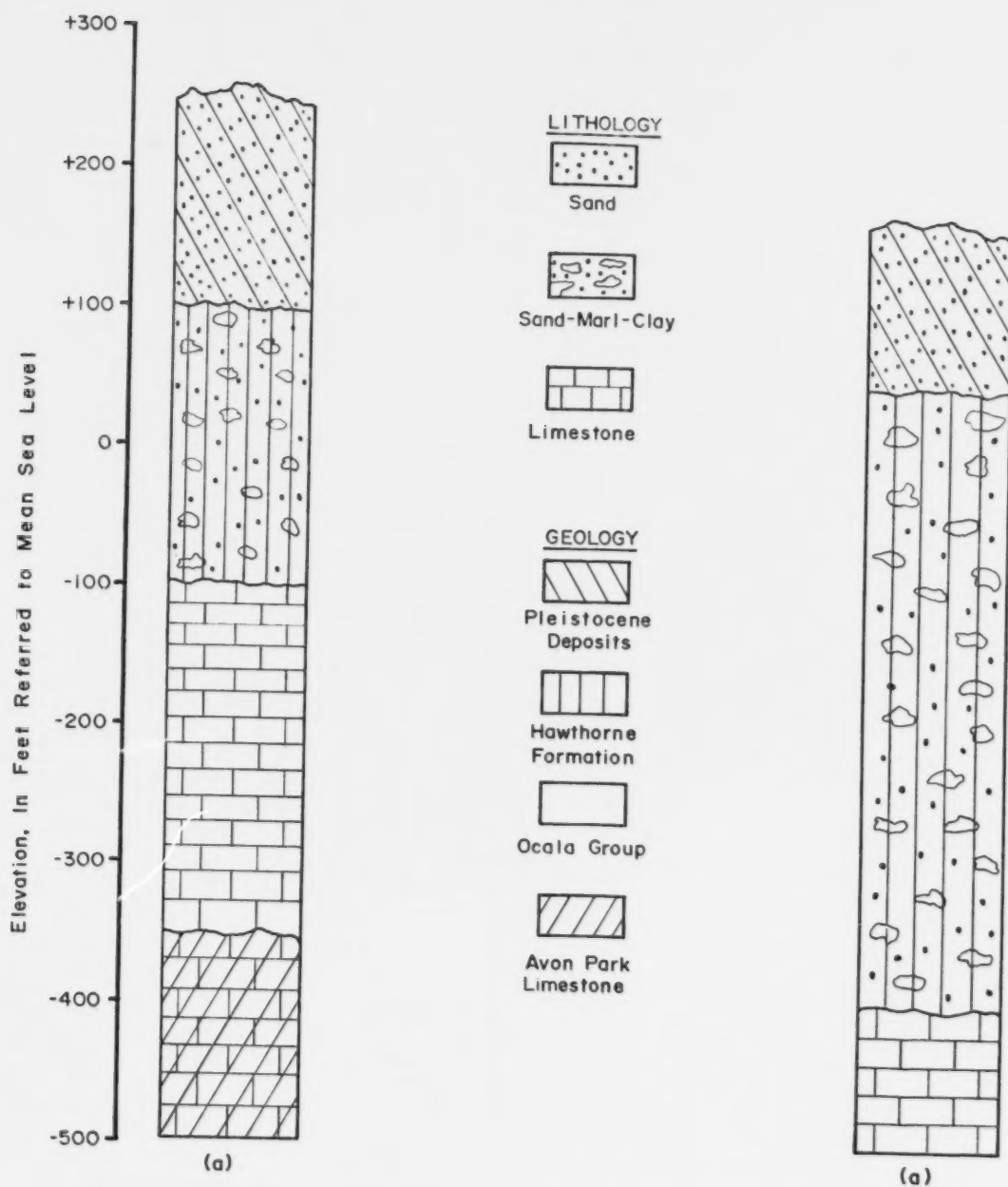


Figure 6-2. Geologic cross-sections of the (a) Trail Ridge Lake District (Clark et al. 1962) and (b) Highlands Ridge Lake District (Bishop 1956).

ft) below mean sea level in the Trail Ridge area and 120 - 150 m (400 - 500 ft) below MSL in the Highlands Ridge.

The relatively thick and impermeable Hawthorne formation (Miocene Age), which consists of thick clays and clayey sands overlying the Ocala Group is a confining bed that holds water under artesian pressure in the Floridan Aquifer. The high terraces that form both the Trail Ridge and Highlands Ridge consist of loose sands deposited on the Hawthorne Formation during interglacial stages of the Pleistocene. The sand deposits forming the surface of the ridges have been reworked by wind and wave action, but ancient sand dunes and sand bars are well preserved.

The lake regions exemplify typical karst topography, with many circular to elliptical basins among the sand hills. Lake basin formation along the ridges results from dissolution of the underlying limestone beds and collapse of the impervious Hawthorne layer and overlying veneer of Pleistocene sands. The basins subsequently fill with water from precipitation, resulting in perched, soft-water lakes in the sand deposits above the confining Hawthorne formation.

Soil Characterization

The sand deposit of the Central Highlands region is classified as an entisol (Asatutula fine sand-quartzipsamment), an excessively drained soil with very high permeability. Native vegetation, reflecting the nutrient-poor status of the sands, consists primarily of mixed turkey and scrub oak and sand pine. A typical soil profile for this region from the surface (A horizon) to 300 cm depth (C6 horizon) generally consists of grey to light-brown fine to coarse sands that are strongly acidic and have a cation-exchange capacity (CEC) of 1 meq/100 g or less and zero percent base saturation (Carlisle et al. 1978). The soil thus has very little neutralization capacity toward acidic precipitation.

Description of individual study lakes

The surface areas and elevations presented in Table 6-1 are from data published by the U.S. and Florida Geological Surveys, Water Resources division or from interpretation of topographic maps. Some of the lakes undergo severe fluctuations in lake stage during times of excess and below-normal rainfall. The severe drought of 1955-57, for example, caused Lake Brooklyn at Keystone Heights to be lowered 7 m (20 ft) and reduced to one-half its normal size (Clark et al. 1964). The areas and elevations given in Table 6-1 are for normal lake stage levels. The lakes are described below in the order they appear in Table 6-1.

1. Lake Altho, located near Waldo in Alachua County, is in the Santa Fe River drainage basin. Lake depth at the mid-lake sampling station was 5 m. The lake drains through the Santa Fe Canal into Little Santa Fe Lake. There is some residential development along the shoreline, but most of the shoreline is lined with cypress that grades rapidly into pine forest in the uplands. The lake is moderately colored because of runoff of humic material from the surrounding forest.

2. Anderson-Cue lake, in Putnam County, is in the Ordway Preserve of the University of Florida. The lake level was low during this study, and its area was reduced by almost 50% compared to the normal 8 ha. Depth at the midlake station during this study was 3.8 m. The lake has no influent or effluent streams and obtains its water from direct precipitation and subsurface seepage. Its small drainage basin is defined by the surrounding high sandhills with elevations of 55 m. There is no human habitation in the drainage basin.
3. Lake Brooklyn in Clay County near the town of Keystone Heights, is the fourth lake in a chain forming the upper Etonia Creek Drainage Basin (Clark et al. 1963). It is underlain by extremely permeable soils, and its level recedes as much as 7 m during years of below average rainfall. During this study the lake was at a very low stage, having received below normal rainfall for several consecutive years. The depth at the sampling station was 5 m. Residential development exists along the south and southwest shore of the lake, while the north shore is relatively free of development.
4. Lake Cowpen in Putnam County also was extremely low during the study (4 m deep at the sampling station) and consisted primarily of several circular pools. Sampling was done at the center of the largest of these pools where there was a public boat ramp. There is some residential development along the shoreline.
5. Lake Galilee is also located in Putnam County approximately 4 km east of Lake Cowpen. Lake Galilee was also low during the sampling period, but its level was less affected by the drought than that of Lake Cowpen was. The depth was 3 m at the mid-lake sampling station. There are a few residents along the south shore of the lake.
6. Lake Geneva is located in Clay County just south of the town of Keystone Heights. The depth at the sampling site was 5.5 m. It is the largest lake (650 ha) in the Etonia Creek Drainage Basin (Clark et al. 1964). It receives drainage from a chain of five upstream lakes during years of average or above average rainfall. Lake Geneva is almost completely surrounded by residential development.
7. Lake Johnson is located in Gold Head Branch State Park in Clay County. It receives influent from Gold Head Branch Creek, which arises from rainfall percolating through sandhills having elevations of 65 m in the immediate area. The lake depth at the sampling station was 3.3 m. The only development along the shoreline is a swimming and picnic area and several rental cottages.
8. Kingsley Lake (Clay County) is 26 m deep at its deepest point and is thought to be the deepest lake in north Florida (Clark et al. 1964). The lake is nearly a perfect circle with an area of 652 ha. Water level fluctuation is small (only ~1 m during the period 1945 to 1963), compared to nearby Lake Brooklyn. There is moderate residential development along the north side of the lake.
9. Lake Lowry (Sand Hill Lake), located in Clay County, is the second of a chain of lakes in the Etonia Creek Basin. It receives flow from Blue Pond,

and its surface outflow goes into Magnolia Lake. The depth at the sampling station was 7 m. The shoreline is completely natural (forest) with the exception of a boat ramp.

10. Lake Magnolia, located near Lake Lowery, is the third lake in the Etonia Creek Basin Chain. During years of average or above average rainfall the lake supplies water to Lake Brooklyn through Alligator Creek. The depth at the sampling station was 15 m. The shoreline also is in a natural state, with no development other than a boat ramp.

11. Lake McCloud (Putnam County) is approximately 750 m northeast of Lake Anderson-Cue in the Ordway Preserve. It is totally enclosed, with surrounding sand hills rising to elevations of 45 m. There are no influent or effluent streams. The lake was low during this study, and the depth at the mid-lake station was 5 m. There is no human habitation in the drainage basin.

12. Lake Santa Rosa (Putnam County) is a sub-circular seepage lake with a normal area of 42 ha. It was also low during this study, and the ends of docks and piers were 10-20 m from the edge of the water. The depth at the mid-lake station was 10 m, but during wetter periods it has a depth of 14-15 m. There are numerous permanent and seasonal cottages in the drainage basin.

13. Lake Sheeler is a small (7 ha) seepage lake near Lake Johnson in Gold Head Branch State Park (Clay County). It is nearly circular with a deep (17 m) conical-shaped basin. The extreme clarity and depth of the lake make it attractive for SCUBA diving, and the park reserves it for this sport. The watershed and shoreline is completely undeveloped except for a trail to the water's edge.

14. Lake Annie (Highlands County) is part of the Archbold Biological Station preserve; its drainage basin is uninhabited and consists totally of native vegetation. The basin is of typical sinkhole formation, being nearly circular and quite deep (20 m). A small stream flows from the north side of Lake Annie into Lake Placid.

15. Lake Clay is approximately 1 km east of Lake June in Highlands County. Sampling was performed at the mid-point of the deepest pool of the lake, where the depth was 7.5 m. Lake Clay drains northward into Josephine Creek, which flows to Lake Istokpoga. Lake Clay is completely surrounded by residential development.

16. Lake Francis, 5 km northwest of the town of Lake Placid (Highlands County) is in the Lake Placid chain of lakes. It receives surface flow from Lakes Placid and June to the south, and drains north through Josephine Creek to Lake Istokpoga. The depth at the mid-lake station was 8 m. The shoreline consists of approximate equal residential development and native vegetation.

17. Lake June or June-in-Winter (formerly Lake Stearns), located in Highlands County, receives water from Lake Placid via Catfish Creek to the south, and its water drains northward through Stearns Creek. The lake is the largest in this study, with an area of 1403 ha. The depth at the mid-lake station was 7 m. Land use along the north and south shorelines is predom-

inantly residential, while citrus groves occupy the eastern shoreline. The west shore is primarily native vegetation.

18. Lake Josephine (Highlands County) is relatively shallow, with the depth at the mid-lake station being 3.5 m. It receives water from Wolf and Jackson Creeks and overflows through Josephine Creek into Lake Istokpoga. Residential development occupies the south side of the lake, and trailer camps occur along the east side. Native vegetation and improved pasture are found to the north.

19. Lake Letta, the northernmost of the Highlands Ridge Group, is located near the town of Avon Park. Lake Letta was low during this study, and the depth at the mid-lake station was 2.5 m. The lake has two inlet streams and drains into Bonnet Lake. The east and north shore of the lake is residential and the southern and eastern shore is dominated by native vegetation.

20. Lake Placid (formerly Lake Childs) is south-southwest of the town of Lake Placid in Highlands County. It is the second largest lake in this survey (1329 ha). It receives water from Lake Annie and drains northward to Lake June. The depth at the mid-lake station was 7.5 m. The shoreline along the western and northern edge is primarily residential, and citrus groves and native vegetation predominate along the eastern and southern shores, respectively.

Previous Lake Studies

Historical data exist for all the study lakes, except Lakes Sheeler and Annie (Table 6-2). Data for some of the Trail Ridge lakes date back over two decades. Clark et al. (1964) reported chemistry data for semi-annual sampling of Lakes Brooklyn, Geneva, Magnolia, Lowery (Sand Hill), Johnson, and Kingsley in the Trail Ridge Lake District. The sampling survey was initiated in 1957, and ended in 1960. Included in the analyses were pH, major ions, and nutrient forms.

Ten years later, the Florida Game and Fresh Water Fish Commission as part of a state-wide survey of Florida lakes reported data on pH, major ions, and nutrients for five Trail Ridge lakes (Brooklyn, Geneva, Lowery, Kingsley, and Altho) and three Highlands Ridge lakes (Francis, June and Letta). Sampling was on an annual basis from 1966 to 1973 (Hennessey and Holcomb 1967; Holcomb 1968, 1969; Duchrow 1970, 1971, 1972; Holcomb and Starling 1973).

Brezonik et al. (1969) conducted intensive sampling of Lakes Anderson-Cue and McCloud in the Trail Ridge District during 1967-68 and reported data on pH, major ions, and nutrients. Sampling was biweekly during 1967 and monthly during 1968.

Shannon (1970) and Shannon and Brezonik (1972) conducted quarterly sampling of 55 north-central Florida lakes during 1969, including all the Trail Ridge lakes in this study, except lakes Johnson and Sheeler.

Milleson (1978) recently conducted a survey of seven lakes in Highlands County, including four lakes studied in this project (Placid, June, Clay, and

Table 6-2. Historical pH, alkalinity and sulfate data for the Trail Ridge Lake Group.

Lake	1957-60*			1968-69**			1967-72 ⁺			1978-79 ⁺⁺		
	pH	Alk. mg/L as CaCO ₃	SO ₄ ²⁻ mg/L	pH	Alk. mg/L as CaCO ₃	SO ₄ ²⁻ mg/L	pH	Alk. mg/L as CaCO ₃	SO ₄ ²⁻ mg/L	pH	Alk. mg/L as CaCO ₃	SO ₄ ²⁻ mg/L
Brooklyn	5.5	2.5	4.1	5.5	0.5	4.0	5.1	0.9	3.2	5.0	0	4.6
Lowery	5.4	2.5	2.0	5.3	0.3	3.8	5.1	0	2.5	5.2	0	3.4
Magnolia	5.6	2.5	2.4	5.5	0.4	3.3				5.1	0	3.0
Geneva	5.4	1.6	5.8	6.3	1.2	5.4	6.1	4.3	6.0	6.1	6.5	9.0
Kingsley	6.3	5.7	4.9	6.9	5.7	5.2	6.6	7.0	5.1	6.7	10.8	7.3
Johnson	5.5	2.5	2.5							5.2	0	2.1
Anderson-Cue				4.8	0	4.4				4.9	0	5.2
Cowpen				5.4	0.4	5.8				4.9	0	13.9
Galilee				5.6	0.6	6.1				5.0	0	11.8
McCloud				4.9	0	4.5				4.7	0	6.8
Santa Rosa				5.2	0.3	4.7				5.1	0	5.3

* Semi-annual sampling during 1957-60 (N=6); Clark et al. (1964).

** Sampling every four months during 1968-69 [N=3; except Anderson-Cue, McCloud (N=6); Geneva, Kingsley (N=5)]; Shannon (1970).

+ Annual sampling 1967-72 (N=6); Holcomb (1968, 1969); Duchrow (1970, 1971, 1972).

++ This study. Sampling during 1978 (N=4).

Josephine). Quarterly sampling was done during 1974-76 and included major ions, pH, and nutrients.

SAMPLING AND ANALYTICAL METHODS

The 20 lakes were sampled on a quarterly basis beginning in spring (April - May) 1978 and ending in winter (January - February) 1979. A mid-lake sampling station was selected in each lake at either the deepest part of the lake or the center of the largest pool, if the lake consisted of several pools. The same station was used on all four sampling dates. Temperature and dissolved oxygen were measured with a YSI Model 51A oxygen meter at three depths in the water column, surface (0.5 m), midway between the surface and bottom, and 1 m from the bottom. Secchi disk transparency also was measured at each sampling station. Water samples for chemical analyses were collected with an acrylic Kemmerer sampler at the same three depths, and a composite sample was taken by mixing equal volumes of water in a plastic bucket. Samples for nutrient analyses were preserved with 1 mL saturated HgCl_2/L , placed on ice in the field, and stored at 4°C. An aliquot of the preserved sample was filtered in the laboratory for analysis of inorganic nutrients. Field pH was measured with an Orion Model 401 Ionalyzer pH meter on the composite sample following standardization of the meter with two buffers (pH 4.0 and 7.0) at ambient water temperature.

Analytical methods for chemical determinations on lake water samples are summarized in Appendix A. Analyses were performed according to standard methods (APHA 1976) and/or the EPA water analysis manual (U.S. EPA 1976). Analyses for organic nutrients, chloride, and sulfate were done by automated methods on an AutoAnalyzer, except for orthophosphate (i.e. soluble reactive phosphate, SRP), which was done manually using the ascorbic acid (single-reagent) method. Total Kjeldahl nitrogen and total phosphate were determined by manual semi-micro digestion of unfiltered samples followed by colorimetric analysis for ammonium (indophenol method on AutoAnalyzer) and orthophosphate (manual single reagent method) on the neutralized digestate.

Samples for chlorophyll analysis were collected at 0.5 m for lakes <5m and at the top, middle, and bottom of the water column for lakes >5 m by a 2.2 L Kemmerer sampler. Samples for lakes >5 m were composited with depth, and a single chlorophyll sample was taken. All samples were placed in opaque plastic bottles and stored in ice. In the laboratory, a minimum of 100 mL of sample was filtered through Whatman 4.25 GF/A glass fiber filters. To the final mL of sample, 5 drops of aqueous saturated magnesium carbonate were added. The filters were placed in glass test tubes containing 5 mL of acetone and ground with a Wheaton tissue grinder. The ground samples were stoppered, and extracted in the dark at -14°C for 24 h. The extracts were filtered through glass fiber filters using a Millipore Swinnex filter attachment and disposable syringes, and the filtrates were brought to final volume of 10 mL with acetone. Absorbance was read on a Beckman DBG spectrophotometer according to standard methods (APHA 1976). Chlorophyll a is the active form of the pigment (i.e. total chlorophyll corrected for phaeophytin [APHA 1976]).

Phytoplankton samples (80 mL) were collected by a 2.2 L Kemmerer sampler at 0.5 m for lakes <5 m and at the top, middle and bottom of the water column

of lakes >5 m. Samples were taken in the center of each lake, placed in screw-cap glass bottles, and preserved with 2 mL of acidified Lugol's solution. In the laboratory, sample aliquots were settled in an Utermohl chamber and identified using a Unitron inverted microscope, using taxonomic keys in Whitford and Schumacher (1968), Cocke (1967), Weber (1971), Prescott (1954), and Smith (1950).

Zooplankton samples were obtained by vertical tow with a number 20 (80 μ m mesh) net through the entire water column near the center of each lake, preserved in 10% buffered formalin, and identified using taxonomic keys in Edmondson (1959) and Pennak (1953). At least 100 individuals were counted in each sample under a dissecting microscope at 250x. Zooplankton biomass was obtained by multiplying the number of individuals for each species by an appropriate biomass conversion factor (Dumont et al. 1975).

Two habitats of benthic invertebrate communities were sampled in each lake. Duplicate grabs were taken at both a shallow-sand station and a deep-mud station. The importance of substrate characteristics in the distribution of benthic communities has been pointed out by Bloom et al. (1972), Parsons (1968), and Mahadevan et al. (1977). Samples were taken with a Ponar grab (Powers and Robertson 1967) with a sampling area of 0.02 m² and a penetration depth of about 10 cm in mud (less in harder substances such as sand). Samples were washed through a 0.66 mm mesh sieve in the field to remove excess sediment. Remaining organisms were preserved in 10% formalin and stained with rose bengal. Samples were sorted in a white pan in the laboratory and identified using both a dissecting and a compound microscope. Biomass measurements were determined for each lake station. All individuals from a single Ponar sample were placed in a tared crucible and dried at 150°C for 24 h to determine dry weights. Ash-free dry weights were determined by combusting samples in a muffle furnace at 550°C for one hour. Statistical analysis was conducted using a package of computer programs developed by Bloom et al. (1977) on an Amdahl 470 at the University of Florida.

RESULTS OF LAKE STUDY: WATER CHEMISTRY

Discussion of the water chemistry of the 20 survey lakes is best accomplished by segregating the lakes into groups according to pH. In the original selection of lakes for study, a geographic grouping (Trail Ridge vs. Highlands Ridge) was used, reflecting the difference in precipitation acidity (Figure 5-1) at the northern (Trail Ridge) site compared to the southern site (Highlands Ridge). A one-way ANOVA with Duncan's multiple range test (SAS; Barr et al. 1976) indicates that the lakes also can be divided into two groups (Figure 6-3) based on pH (i.e. acidic and non-acidic). The boundary pH between the two groups is 5.6, which coincidentally is the geochemical equilibrium pH of pure water in contact with atmospheric CO₂. The grouping based on pH compares closely with the geographical grouping (Table 6-1), except that the three largest lakes of the Trail Ridge group, Kingsley, Geneva, and Altho, were grouped with the Highlands Ridge lakes. These three Trail Ridge lakes have higher pH levels than the other Trail Ridge lakes, possibly because of their size, depth, and extent of shoreline development. The following discussion thus divides the 20 lakes into two groups: an acidic lake group (pH < 5.6) and a non-acidic group (pH > 5.6).

<u>Grouping</u>		<u>Mean pH</u>	<u>N</u>	<u>Lake</u>	
	A	6.795	4	Francis	NONACID LAKE GROUP
	A				
	A	6.742	4	Kingsley	
	A				
	A	6.710	4	Clay	
	A				
	A	6.670	4	June	
	A				
	A	6.535	4	Placid	
	A				
	A	6.497	4	Letta	
	B	6.145	4	Geneva	GROUP
	B				
	B	6.142	4	Josephine	
	B				
C	B	6.025	4	Alto	
C					
C		5.752	4	Annie	
	D	5.245	4	Johnson	ACID LAKE GROUP
	D				
E	D	5.195	4	Lowery	
E	D				
E	D	5.140	4	Sheeler	
E	D				
E	D	5.097	4	Magnolia	
E	D				
E	D	5.057	4	Rosa	
E	D				
E	D	F 5.025	4	Brooklyn	GROUP
E	D	F			
E	D	F 4.980	4	Galilee	
E	D	F			
E	D	F 4.940	4	Anderson Cue	
E		F			
E		F 4.857	4	Cowpen	
E		F			
		F 4.715	4	McCloud	

Figure 6-3. Duncan's multiple range test for the annual mean pH of the survey lakes. Mean lake pH values with the same letter are not significantly different at the .05 level.

Lake Transparency

As discussed earlier, the lakes located along the Trail and Highlands Ridges were formed in basins consisting of sandy deposits, and they have little or no input of surface runoff. Thus these lakes have the most transparent waters of all lakes in the state. Except for two highly colored lakes, Altho and Josephine, which had mean annual color levels of 194 and 154 CPU, most of the lakes had color values of 20 CPU or less. Both Altho and Josephine are atypical of the other Ridge lakes in that cypress wetlands are located within their watersheds, and colored water containing humic material flows from these swampy areas into the lakes. Lowest color concentrations were recorded for two pristine, extremely clear lakes, Sheeler (5 CPU) and Annie (7 CPU). Average turbidity levels also were very low in the lakes, ranging from 0.6 NTU (Sheeler and Cowpen) to 4.9 NTU (Josephine). Values for most of the lakes were less than 2 NTU.

As expected for lakes with low color and turbidity levels, transparency (Secchi disk) values were high. For example, Lakes Sheeler, Santa Rosa, and Magnolia (in the Trail Ridge group) had average Secchi transparency depths of 7.9, 5.9, and 5.3 m, respectively. Lake Annie (in the Highlands Ridge) has an average Secchi depth of 5.5 m. The two colored lakes, Altho and Josephine, had the lowest mean Secchi values of all the lakes, 1.0 and 0.67 m, respectively. Greatest Secchi depth values generally were recorded in the winter and spring months. Water levels for several of the Trail Ridge lakes were at a 20-year low as a result of several years of below normal rainfall. Consequently, the Secchi disk sometimes was visible resting on the bottom of some of the lakes. This was particularly true for Lakes Cowpen and McCloud.

Major Ion Composition

The ionic composition of surface waters is a function of contributions from surface and subsurface runoff within the drainage basin, atmospheric precipitation, and the balance between evaporation and precipitation. In soft-water lakes such as those of the Trail and Highlands Ridge districts, the relative abundance of cations and anions is often given as (Wetzel 1975):

Cations: $\text{Na}^+ > \text{Ca}^{+2} > \text{Mg}^{+2} > \text{K}^+$;

Anions: $\text{Cl}^- > \text{SO}_4^{-2} > \text{HCO}_3^-$

Table 6-3 lists the mean concentrations and standard deviations of major ions in the two lake groups, and Figure 6-4 presents the average contributions of the major ions to the total cation and anion equivalents. For each parameter listed in Table 6-3 there is a statistically significant difference between the mean values in each lake group. The ionic bar graphs show good agreement between the sums of the major cation and anion equivalents. Additionally, theoretical conductivities were calculated from the mean ionic composition of each lake group. These values compare closely to the mean measured conductivities for the two groups:

Table 6-3. Means and standard deviations of major ions and specific conductance in the two lake groups.

Parameter	Acidic Group* 10 Lakes (N=40)	Non-acidic Group* 10 Lakes (N=40)
H ⁺ $\mu\text{g/L}$	10.5 $\pm$ 5.0 (pH 4.98)	0.62 $\pm$ 0.62 (pH 6.21)
Specific Conductance $\mu\text{S/cm @ } 25^{\circ}\text{C}$	41.5 $\pm$ 18.2	92.9 $\pm$ 39.8
Na ⁺ mg/L	2.88 $\pm$ 1.27	5.92 $\pm$ 2.13
Ca ⁺² mg/L	0.99 $\pm$ 0.75	3.67 $\pm$ 1.52
Mg ⁺² mg/L	0.54 $\pm$ 0.27	2.15 $\pm$ 1.36
K ⁺ mg/L	0.57 $\pm$ 0.35	2.03 $\pm$ 1.67
Al(III) $\mu\text{g/L}$	58 $\pm$ 29	23 $\pm$ 15
Cl ⁻ mg/L	5.51 $\pm$ 1.94	11.10 $\pm$ 3.55
SO ₄ ⁻² mg/L	5.51 $\pm$ 1.94	13.01 $\pm$ 6.51
HCO ₃ ⁻ mg/L	0	8.66 $\pm$ 5.28

*Means for the two groups are significantly different ($P < 0.0001$ in each case) for each parameter, based on one-way ANOVA (Barr et al. 1976).

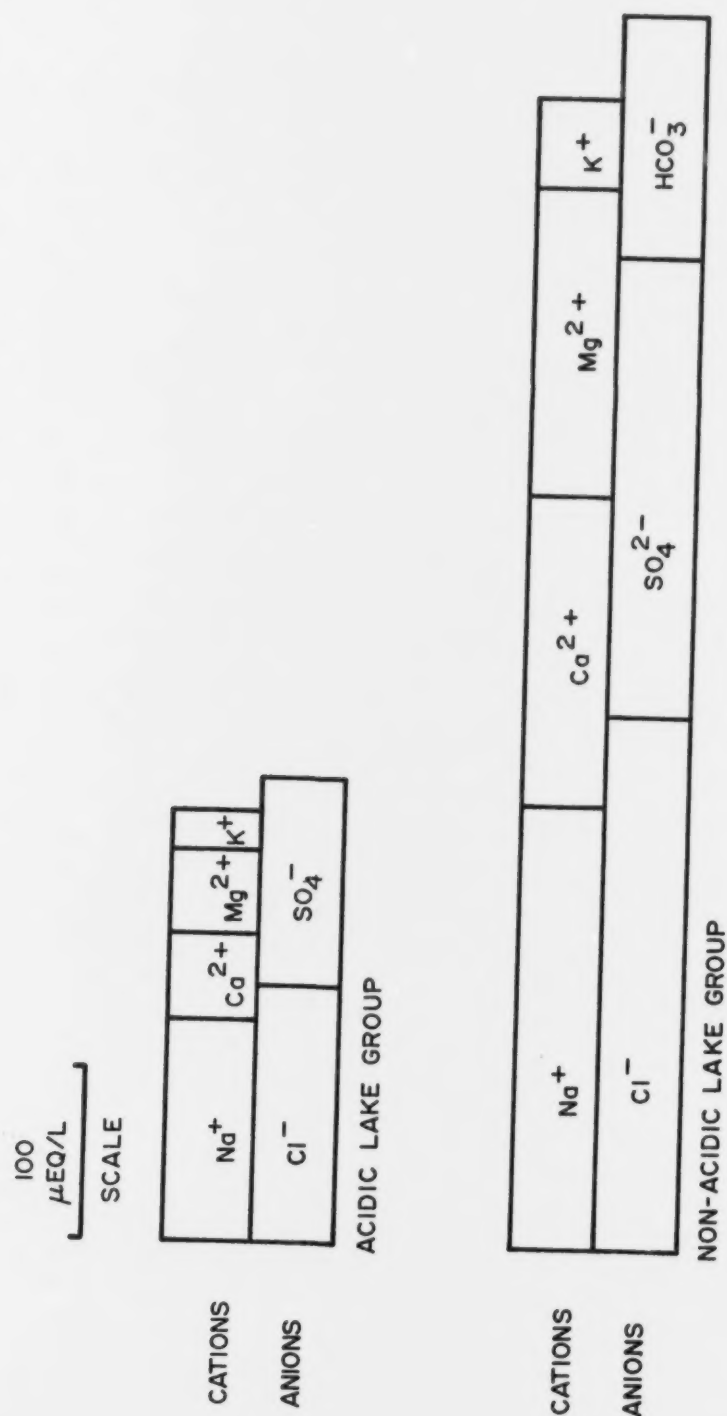


Figure 6-4. Average ionic composition of the acidic and non-acidic lake groups. Lengths of bars in μeq/L.

Specific Conductance
 $\mu\text{S/cm}$ (at 25°C)

	<u>Actual</u>	<u>Calculated</u>	<u>% Error</u>
Acidic Group	41.5	38.2	8%
Non-acidic Group	92.9	89.3	4%

The bar graphs in Figure 6-4 illustrate that, on an equivalents basis, the order of dominance of cations in both groups of lakes was the same as that given above for typical softwater lakes. The cations in both lake groups were dominated by sodium on both a mg/L and a $\mu\text{eq/L}$ basis. Sodium comprised 50 and 39% of the cationic equivalents in the acidic and non-acidic groups, respectively. The relative contributions of calcium (20%) and magnesium (18%) were approximately equal in the acidic group, as well as in the non-acidic group (Ca (27%) and Mg (26%)). Potassium is the least important of the major cations and contributes 6-8% of the cationic equivalents in the two groups. Hydrogen (H^+) and aluminum ion provide small contributions (< 5% each) to the cation equivalents of the acidic lake group.

The major anions in the acidic lake group are chloride (Cl^-) and sulfate (SO_4^{2-}), which comprise 57 and 43% of the total anion equivalents, respectively. In the non-acidic group the major anion species are Cl^- (43%), SO_4^{2-} (37%) and bicarbonate, HCO_3^- (20%), but there is no contribution by HCO_3^- to the anion component of the acidic group. The low bicarbonate levels that existed in these lakes in the 1950s and 1960s have been titrated by inputs of acidic precipitation over the last decade. This matter is discussed in greater detail in the section dealing with historical lakewater chemistry trends.

Specific conductance values for the survey lakes were low, as expected for softwater lakes. All the lakes had annual mean values less than 150 $\mu\text{S/cm}$, and 9 of the 20 lakes had mean values less than 50 $\mu\text{S/cm}$ (Figure 6-5). The mean conductivity for the acidic group was 41.5 $\mu\text{S/cm}$ (range of 19 to 78 $\mu\text{S/cm}$). For the non-acidic group the mean was 92.9 $\mu\text{S/cm}$ (range of 35 to 147 $\mu\text{S/cm}$). As shown in Figure 6-5 the lakes with the higher pH values also tended to have higher conductivity values, indicating somewhat harder, more buffered waters.

The mean pH of the acidic lake group was 4.98, and annual means ranged from 4.71 (McCloud) to 5.21 (Johnson). The mean for the non-acidic group was 6.21, and annual means ranged from 5.73 (Annie) to 6.70 (Clay). The lowest measured pH during the study was 4.60 for McCloud (winter), while the highest value was 7.02 for Francis (fall). Seasonal variations generally were less pronounced for the acidic lake group than the non-acid group. The very acidic Lake McCloud, for example, had pH values that ranged from 4.60 (winter) to 4.82 (spring), while Lake Francis, a non-acid lake, had pH values ranging from 6.35 to 7.02 (spring and fall, respectively). The larger seasonal fluctuations of pH in the non-acidic lakes likely reflect higher productivities in these lakes than the acidic lakes.

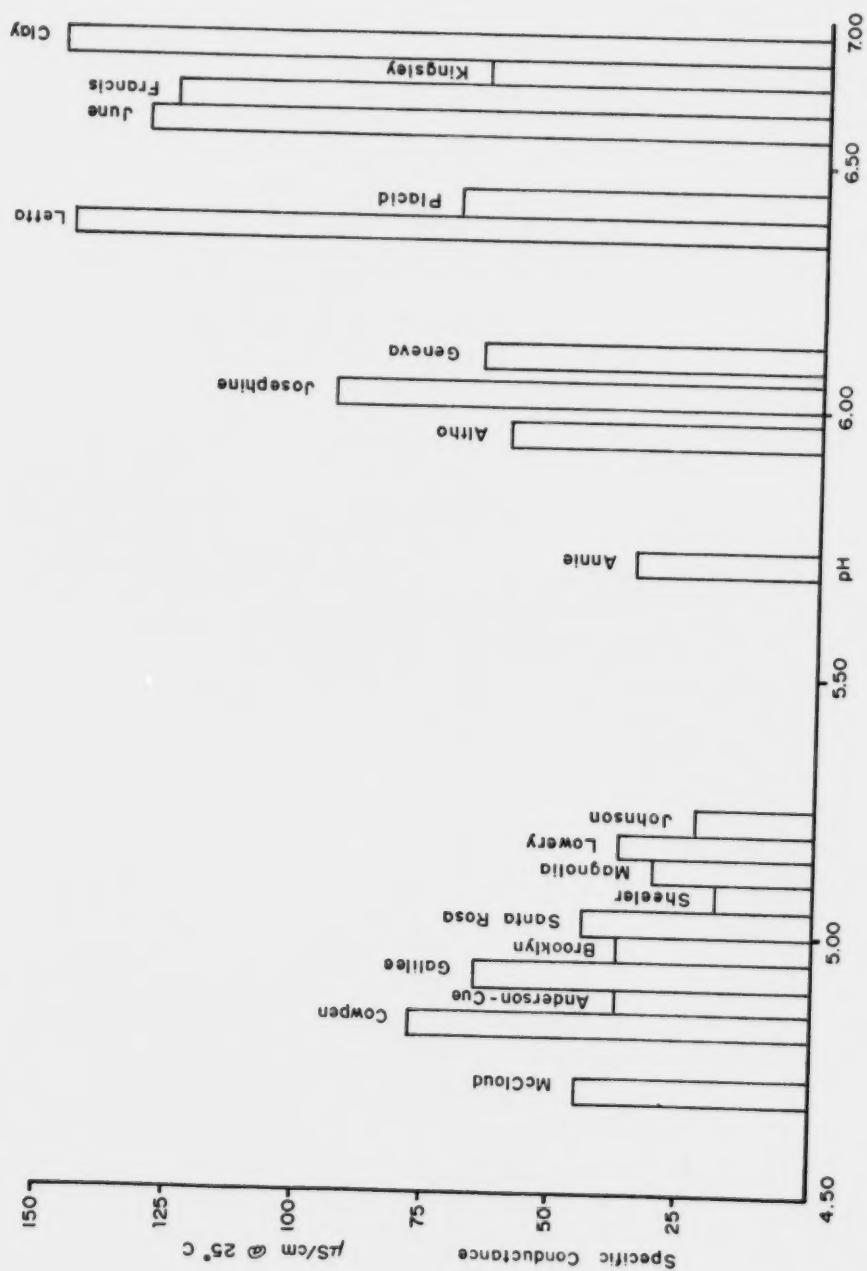


Figure 6-5. Average levels of specific conductance in the 20 study lakes plotted vs. average p H.

Nutrients

To properly assess the effect of acidification on the biota and productivity of the survey lakes it is necessary to consider nutrient levels in the lakes. The most important nutrients controlling the productivity of lakes are phosphorus and nitrogen. Silica concentrations can be important in controlling algal species composition, i.e. in limiting the growth of diatoms.

Table 6-4 presents the means and standard deviations of major phosphorus forms in each lake group. In the acidic lake group, annual average soluble reactive phosphate (SRP) levels ranged from 4 (Sheeler) to 18 $\mu\text{g/L}$ (Anderson-Cue), and total phosphate (TP) concentrations ranged from 7 (Sheeler) to 40 $\mu\text{g/L}$ (Anderson-Cue). In the non-acidic group, SRP ranged from 4 $\mu\text{g/L}$ (Annie) to 27 $\mu\text{g/L}$ (Josephine), while the average TP concentration ranged from 8 $\mu\text{g/L}$ (Annie) to 68 $\mu\text{g/L}$ (Josephine). Statistical analysis (ANOVA) showed no significant differences (0.05 level) between the mean SRP concentrations in the two lake groups but a significant difference was found for the TP and organic P levels (Table 6-4).

Mean values and standard deviations for the major forms of nitrogen in the two lake groups are listed in Table 6-4. Average inorganic nitrogen concentrations (in mg N/L) in the acid lake group ranged from 0.037 (Cowpen) to 0.37 (Anderson-Cue), while the range in the non-acid group was 0.026 (Annie) to 0.11 (Placid). Organic nitrogen levels (in mg N/L) ranged from 0.10 (Cowpen) to 0.46 (Anderson-Cue), while the range in the non-acid group was 0.23 (Annie) to 0.68 (Josephine) for the non-acid lakes. Statistically significant differences between the means of each group were not found (Table 6-4) for inorganic species (NH_4^+ , and NO_3^- , but TON and TN levels were different (at the 0.0001 and 0.005 levels, respectively).

Silica concentrations can be important in controlling productivity in fresh waters especially if the phytoplankton population is composed largely of diatoms. As shown in Table 6-4, the mean values of SiO_2 in the two lake groups are similar, and the large standard deviations for each mean indicate considerable scatter in SiO_2 concentrations within the groups. For example, SiO_2 mean concentrations ranged from 51 (Cowpen) to 950 $\mu\text{g/L}$ (Lowry) in the acid lake groups, and in the non-acid group silica ranged from 115 (Geneva) to 1180 $\mu\text{g/L}$ (Josephine). Consequently, statistical analysis indicated no significant differences in mean SiO_2 between the two groups of lakes.

Since significant differences were found in the mean levels of organic constituents (TON, organic P, TOC) and total nutrients (TN, TP) between the two lake groups (Table 6-4), the non-acidic lakes (with higher values for these parameters) would appear to be more productive than the acidic lakes. As discussed later, the difference in chlorophyll a levels between the two lake groups support this conclusion. Reasons for the increased levels of total and organic nutrients in the non-acidic lakes are not certain, but the difference may reflect lower rates of mineralization in acidic waters. On the other hand, the lower nutrient concentrations may simply reflect lower nutrient loading rates to the acidic lakes, many of which are in small, pristine watersheds. Further studies are necessary to evaluate these alternative explanations.

Table 6-4. Means and standard deviations of nutrients in the two lake groups.

Parameter	Acidic Group 10 lakes (N=40)	Non-acidic Group 10 lakes (N=40)	Probability* means are not different
$\text{NH}_4^+\text{-N}$ $\mu\text{g/L}$	72 $\pm$ 99	41 $\pm$ 48	.0812
$\text{NO}_3^-\text{-N}$ $\mu\text{g/L}$	21 $\pm$ 41	16 $\pm$ 17	.4158
TON $\mu\text{g/L}$	199 $\pm$ 131	405 $\pm$ 193	.0001
TN $\mu\text{g/L}$	292 $\pm$ 219	462 $\pm$ 196	.0005
SRP $\mu\text{g/L}$	7 $\pm$ 6	10 $\pm$ 11	.0940
TP $\mu\text{g/L}$	16 $\pm$ 12	26 $\pm$ 22	.0109
ORG P $\mu\text{g/L}$	9 $\pm$ 9	16 $\pm$ 19	.0353
TOC mg/L	4.6 $\pm$ 3.4	7.0 $\pm$ 3.9	.0039
SiO_2 $\mu\text{g/L}$	459 $\pm$ 341	420 $\pm$ 416	.6481

*Probabilities listed are from ANOVA (Barr et al. 1976) on the annual means for each parameter in each group. If $P \leq .05$, means are accepted as statistically different.

Aluminum

Atmospheric inputs of acidity (H_2SO_4 and HNO_3) to the drainage basins of lakes result in increased weathering and mobilization of metals within the watersheds of the lakes. In non-calcareous soils, increased deposition of acidity leads to increased concentrations of dissolved aluminum in surface and ground waters (Cronan and Schofield 1979; Gjessing et al. 1976). An important ecological consequence of increased aluminum levels in lake waters is the loss or diminution of game fish populations because of the toxic effect of free aluminum ion (Al^{3+}) and its hydroxo-complexes (AlOH^{2+} , $\text{Al}(\text{OH})_2^+$). Laboratory studies have shown that brook trout exhibit a toxic response when aluminum levels are above 200 $\mu\text{g/L}$ in the pH range 4.4 to 5.9.

Since the watersheds of the Trail and Highlands Ridge lakes are typically non-calcareous, aluminum analyses were included in the chemical determinations of the lakes. Average annual and maximum aluminum concentrations were found to vary with the mean lakewater pH (Figure 6-6). Highest aluminum levels were found in the lakes with the lowest mean pH values. The average aluminum concentration for the acidic lake group was 58 $\mu\text{g/L}$, and the mean for the non-acidic group was 23 $\mu\text{g/L}$. These mean values are statistically different at the 0.0001 level (Table 6-3). The mean aluminum concentrations ranged from 116 (Cowpen) to 33 $\mu\text{g/L}$ (g/L (Sheeler) in the acidic lake group and 43 (Annie) to 24 $\mu\text{g/L}$ (Geneva) in the non-acidic group. The highest Al concentration found during the survey was 150 $\mu\text{g/L}$ in Lake Cowpen in winter of 1978. Since precipitation contains very little aluminum ($< 10 \mu\text{g/L}$), the aluminum levels in the lakes have resulted from leaching of soils within the watersheds.

Analysis of historical trends in chemical composition of lakes

Water chemistry data on some of the lakes in the Trail Ridge region are available for over a 20-year period, and thus it is possible to examine the results of the present lake survey in a historical context. However, it should be pointed out that in most cases the historical record is rather sparse. No measurements are available for many years, and the number of samples collected in any year was very small (one or two) for most of the historical studies. Table 6-2 lists data on pH, alkalinity (mg/L as CaCO_3), and sulfate for eleven of the Trail ridge lakes in a generally chronological sequence. There apparently are no historical data on Lake Sheeler. The parameters were chosen for historical comparison because they most likely would reflect lakewater chemistry changes brought about by increased deposition of acidic precipitation. Approximately 70% of the free acidity in precipitation in Florida is H_2SO_4 (see Chapter 5). The data indicate that changes in water chemistry have occurred for all the lakes within the time period of the data. Except for Lakes Geneva and Kingsley, the lakes show a decrease in pH and/or alkalinity, presumably due to atmospheric inputs of sulfuric and nitric acids. Increases in the SO_4^{2-} content of the lakes are also evident for most of the lakes. Interestingly, Lakes Geneva and Kingsley show increases in both pH and alkalinity over the past 20 years. These lakes are the largest of the Trail Ridge lakes (Table 6-1), and they have experienced extensive shoreline development during this time. Previous data for Lakes June, Francis, and Letta (Highlands Ridge) collected during 1967-72

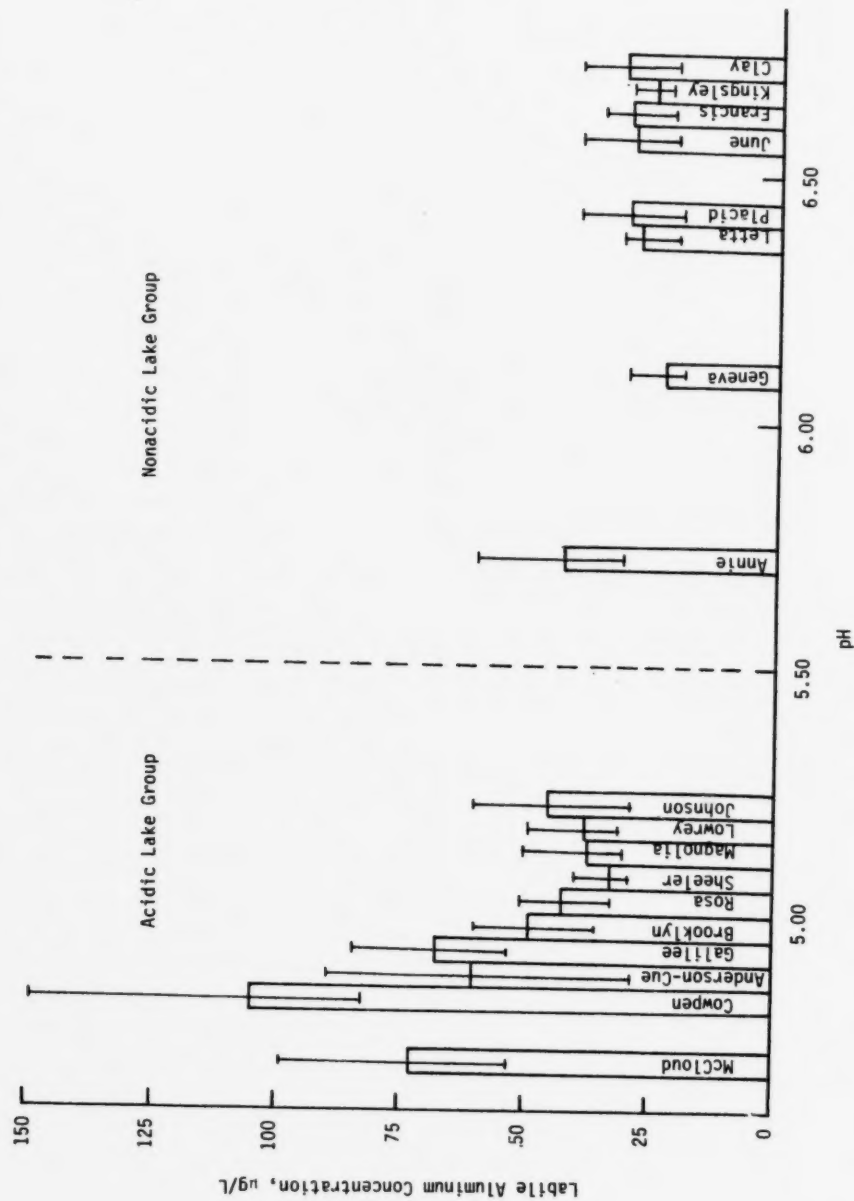


Figure 6-6. Average and range of labile aluminum in the 20 study lakes plotted vs. pH.

(Holcomb 1968,69; Duchrow 1970,71,72)(Table 6-2) indicate these lakes have shown little change in pH and alkalinity over the last 10 years.

It has been estimated (Likens et al. 1979) that lakes with about 80 $\mu\text{eq/L}$ of HCO_3^- (alkalinity equal to 4.0 mg/L as CaCO_3) and a pH of approximately 6.5 will lose their bicarbonate buffer to the point where the lakewater pH drops below 5, if the long-term mean pH of precipitation is about 4.3. Less acidic precipitation could bring about similar changes in lakes with originally lower bicarbonate levels. As shown in Table 6-2, the alkalinity of the soft-water Trail Ridge lakes essentially has been completely titrated by acidic precipitation. Consequently, these lakes are very sensitive to further acidic inputs.

RESULTS OF LAKE SURVEY: BIOLOGICAL COMMUNITIES

Phytoplankton and Chlorophyll

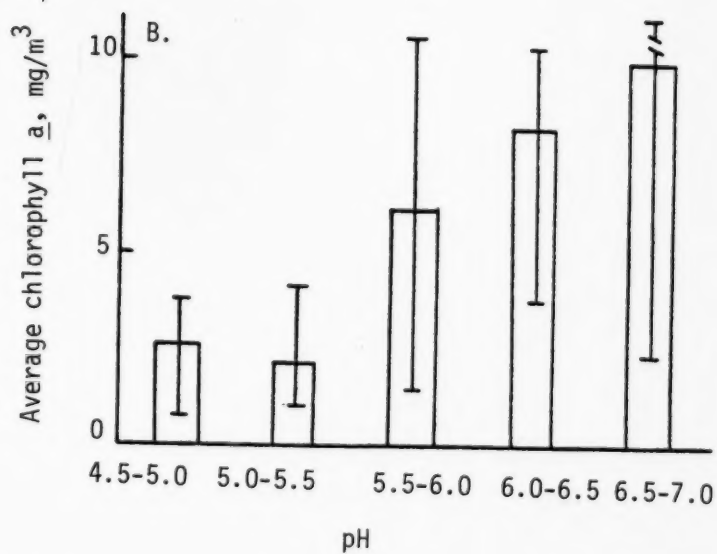
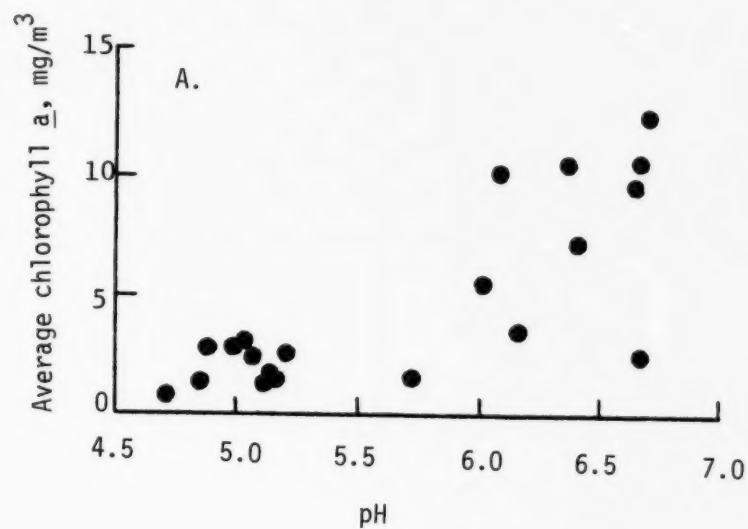
As the base of the aquatic food chain, phytoplankton are an essential component of lake ecosystems. Variations in the number of individuals, in species richness, or in productivity may affect all trophic levels. Reported effects of increased acidity on phytoplankton communities include a decline in species richness, a reduction in algal abundance, decreased algal productivity, and a replacement of blue-green algae by green algae as the dominant phytoplankters (Lackey 1938; Leivestad et al. 1976; Yan and Stokes 1978).

The concentration of total phosphorus (TP) is important to the productivity of phytoplankton communities (Vollenweider 1968). The mean TP concentration in the 10 acidic lakes was 15 $\mu\text{g/L}$, whereas the less acidic group had a mean of 26 $\mu\text{g/L}$ (Table 6-4). The concentration of phosphorus in lake water may be decreased by lowering pH because rates and efficiencies of nutrient recycling from organic matter may be lower under acidic conditions (Grahm 1976). However, most of the lakes in the nonacid group are in watersheds with moderate cultural development (including some orange groves). Watersheds of lakes in the acidic group generally have less cultural development, and the lower concentrations of TP in the acidic lakes thus are likely due to a combination of acidity effects and reduced cultural impact.

1. Chlorophyll a

Mean annual chlorophyll a concentration (corrected for phaeophytin) from the 10 acidic lakes (Table 6-5) was 2.74 mg/m^3 , and the mean for the 10 non-acidic lakes was 10.0 mg/m^3 . Concentrations of chlorophyll a decreased with decreasing pH (Figure 6-7a), although the data exhibit a fair amount of scatter. The mean chlorophyll a concentration in 5 pH intervals (Figure 6-7b) more clearly demonstrates the definite trend of decreasing chlorophyll a with decreasing pH. Based on a Kruskal-Wallis rank sum test, the lakes had statistically different concentrations of chlorophyll a ($\alpha = .005$).

In addition to a pH-chlorophyll relationship, a phosphorus-chlorophyll relationship also can be discerned in Figure 6-8. However, the absence of lakes with low pH and high TP concentrations in the sample group precludes the



Number of Lakes	4	6	2	4	4
-----------------	---	---	---	---	---

Figure 6-7. Annual average chlorophyll a vs. pH (A) and as means of lakes within five pH intervals (B) for the 20 survey lakes.

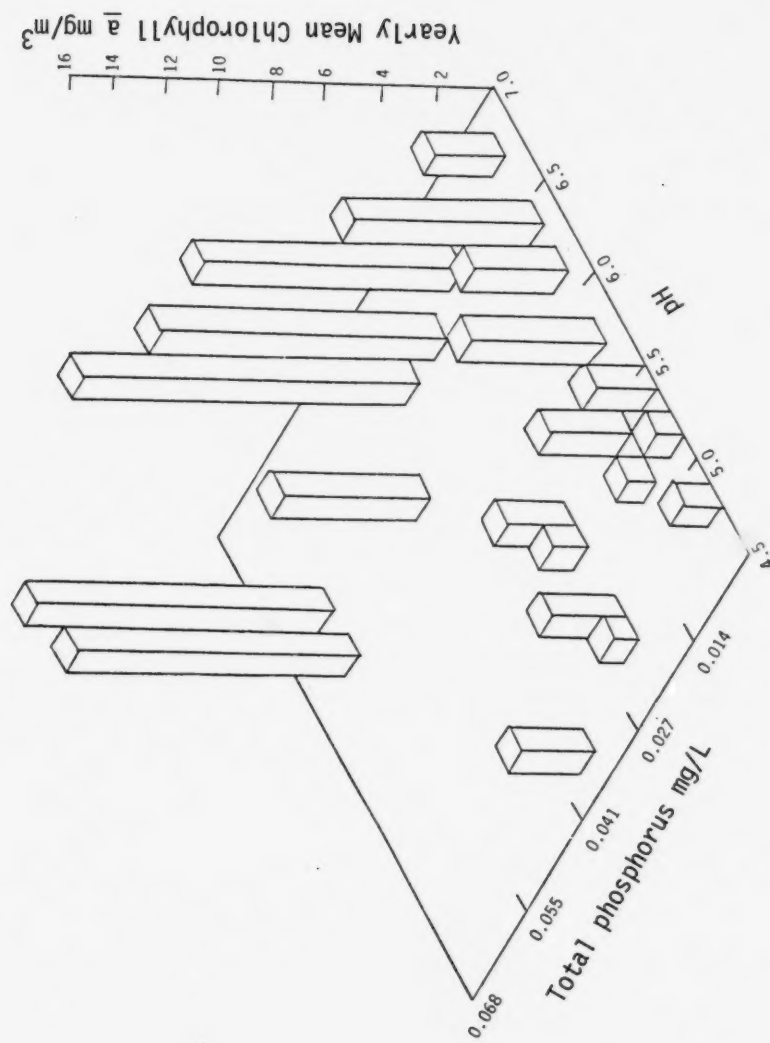


Figure 6-8. Three dimensional plot of chlorophyll a level as a function of pH and total phosphate levels in the 20 lakes.

definition of a response surface of pH, TP, and chlorophyll a over the pH range (4.5 - 7.0) of the data base. A sufficient range of TP values exists for lakes with relatively high pH (i.e. values > 6.0) to demonstrate an overall trend of increasing chlorophyll with increasing TP.

2. Species Richness and Abundance of Phytoplankton

The number of phytoplankton species per sample decreased with pH (Table 6-5), but as shown in Figure 6-9a, a considerable amount of scatter exists in the relationship, especially for lakes with pH > 6.0. In the less acidic lakes, (H^+) exerts less control over phytoplankton community than in lakes of lower pH. Based on a Kruskal-Wallis rank sum test, the 20 lakes had statistically different numbers of phytoplankton species ($\alpha = .005$).

The mean number of species in the 10 acidic lakes (pH < 5.2) was 10.8 (range of 8 to 13), and the mean number of species in the non-acidic lakes (pH > 5.7) was 16.5 (range of 11 to 22). By grouping the 20 lakes into five pH intervals (Figure 6-9c), the decrease in number of species with decreasing pH is depicted more clearly. The mean number of species increased progressively from 10.5 in the most acidic group of lakes to 17.0 in the least acidic group of lakes.

Similarly, the number of phytoplankton individuals decreased with decreasing pH (Figure 6-9b), but again the data are highly scattered. According to a Kruskal-Wallis rank sum test, the 20 lakes had statistically different phytoplankton abundances ($\alpha = .0005$). The mean number of individuals from the 10 acidic lakes was 5,670/mL (range of 2,940 to 10,900/mL). The mean number of individuals from the nonacidic lakes was 14,000/mL (range of 4,730 to 25,600/mL). The mean number of phytoplankton individuals in each of the 5 pH intervals (Figure 6-9c) more clearly illustrates the increase in the number of individuals in the pH range of 6.0 - 7.0.

The isometric plot in Figure 6-10 illustrates the dependence of phytoplankton abundance on both pH and TP concentration. The absence of lakes with low pH and high TP in the data base again precludes definition of the complete response surface. Based on available data, phytoplankton abundance increased with increasing pH at all levels of TP in the 20 study lakes. A similar but less complete trend of increasing phytoplankton abundance with increasing TP was observed at all pH intervals.

The consistently low TP levels in all acidic lakes except Anderson-Cue, plus reports in the literature of decreased recycling of nutrients in acidic lakes suggest a causal relationship between the low TP concentrations and low pH of the lakes. Anderson-Cue lake was the site of a previous eutrophication experiment (Brezonik et al. 1969) and received relatively high inputs of phosphorus for several years. Further studies are needed to define the relationship among phosphorus, chlorophyll, and lake acidity.

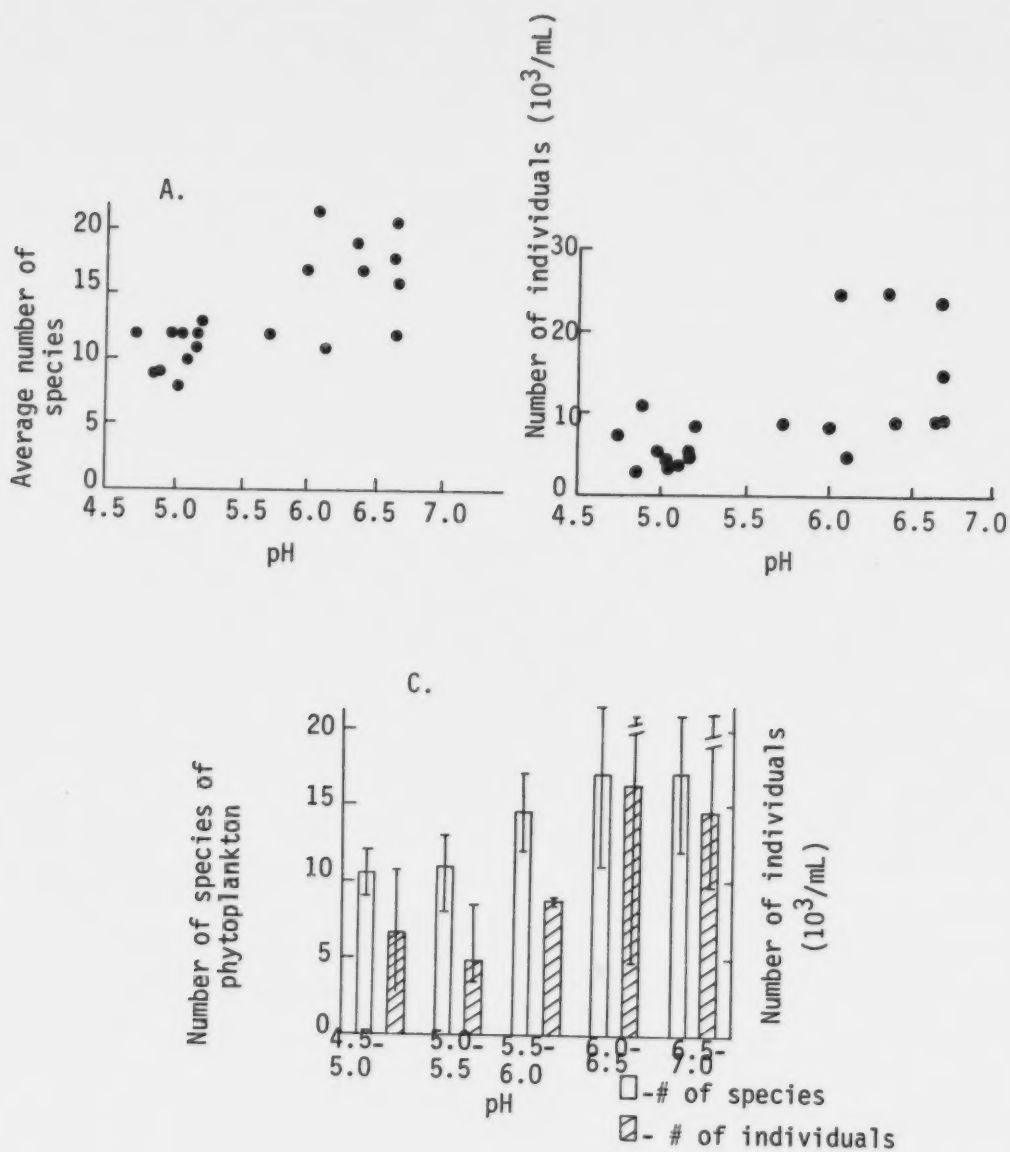
3. Species Composition

One of the most obvious changes in the composition of phytoplankton communities, both in previous studies (Yan 1975) and in the present investiga-

Table 6-5. Summary of phytoplankton data for the 20 study lakes.¹

Lake	pH	Number of Species	Individuals (#/mL)	Chlorophyll <u>a</u> mg/m ³
McCloud	4.71	12	7,340	0.9
Cowpen	4.84	9	2,940	1.3
Anderson-Cue	4.89	9	10,870	2.8
Galilee	4.96	12	5,650	2.9
Brooklyn	5.01	8	4,330	3.0
Rosa	5.05	12	3,390	2.2
Sheeler	5.09	11	3,730	1.0
Magnolia	5.10	10	5,460	1.1
Lowery	5.19	12	4,510	1.1
Johnson	5.20	13	8,520	2.5
Annie	5.72	12	8,890	1.5
Altho	6.00	17	8,680	5.5
Josephine	6.07	22	25,580	11.0
Geneva	6.12	11	4,730	3.5
Letta	6.37	19	24,540	10.5
Placid	6.40	17	9,590	7.2
June	6.64	18	9,720	9.7
Francis	6.66	21	24,160	10.9
Kingsley	6.68	12	9,070	2.7
Clay	6.69	16	15,080	12.7

¹Mean values for four sampling periods



Number of
lakes

4 6 2 4 4

Figure 6-9. Average number of species (A) and number of individuals (B) of phytoplankton vs. pH and bar graphs (C) of average number of species and average number of individuals per lake within five pH intervals for the 20 survey lakes.

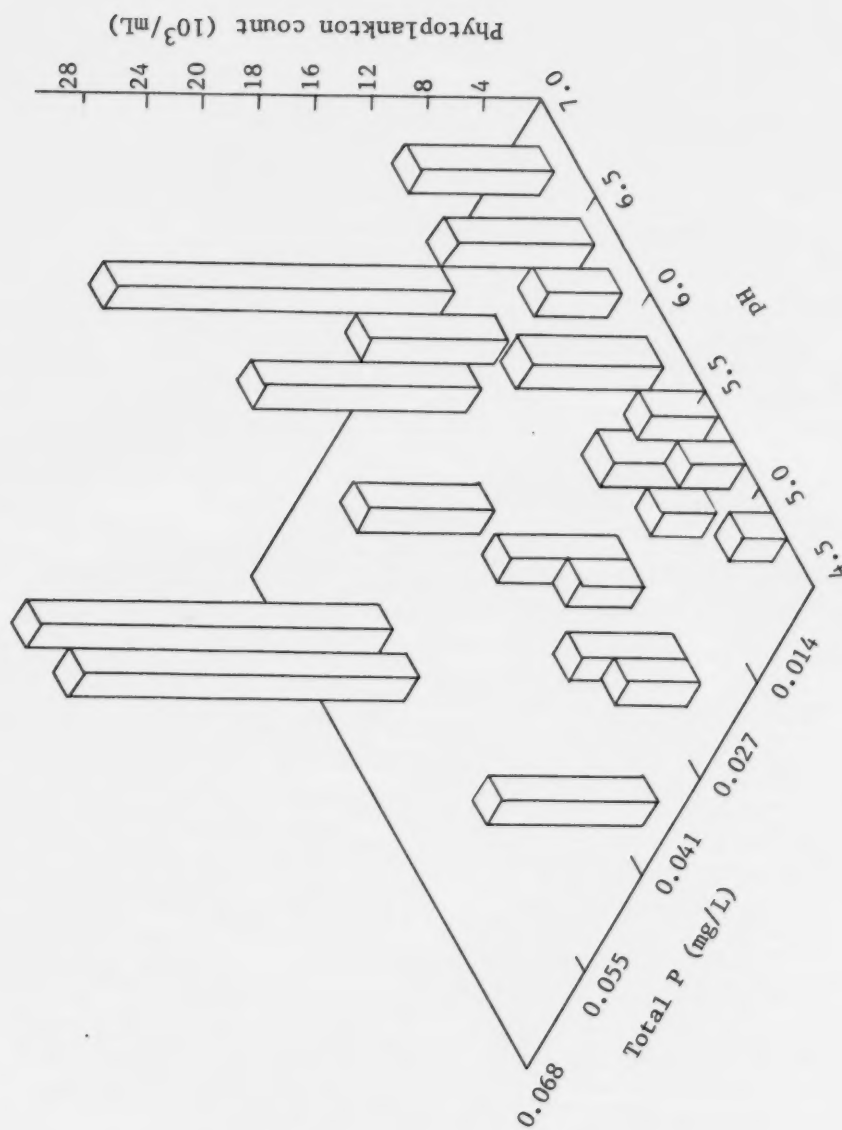


Figure 6-10. Three dimensional plot of phytoplankton density as a function of pH and total phosphate levels in the 20 survey lakes.

tion, is a replacement of blue-green algae as the dominant group at high pH by green algae as the dominant group at low pH. In lakes of pH 4.5 - 5.0 (Figure 6-11), green algae made up 60% of the total number of phytoplankton individuals, while blue-green algae contributed 25%. In lakes of pH 6.51 - 7.0, green algae were responsible for 31%, while blue-green algae made up 63% of the total number of individuals. Similar results were obtained by Yan and Stokes (1978), who found an increase in the ratio of green algae to blue-green algae with increasing acidity.

A decrease in the number of rare species was strongly associated with decreasing pH, as shown in the species list in Table 6-6. Highly acidic lakes were dominated by Staurastrum spp., Scenedesmus sp., Ankistrodesmus falcatus, Peridinium inconspicuum and several species of small coccoid green algae. Blue-green algae were sparse in the acidic lakes and were represented mainly by Oscillatoria limnetica and Anacystis incerta. Other algae found in the acidic lakes included Euglena sp., Oocystis spp. and Chlamydomonas sp. Diatoms were also rare in the acidic waters, with Tabellaria sp. as the dominant genus and Navicula and Melosira as the principal subdominants. The nonacidic Florida lakes contained more rare species and greater numbers of blue-green species such as Amigdalum quadridentata, Anabaena spp., Spirulina laxissima and Microcystis aeruginosa. The species composition of the study lakes was similar to that for lakes of comparable pH reported in the literature. Almer et al. (1974) found Chlamydomonas sp., Peridinium inconspicuum, and Oocystis sp. as the dominants in acidified lakes of Scandinavia.

The overall effects of increased acidity on the phytoplankton communities of Florida lakes thus include a reduction in number of species and individuals and lower chlorophyll a. Blue-green algae were found to be dominant in nonacidic lakes, while green algae were the most common group in the acidic lakes. The effects of pH on the phytoplankton community are confounded in part by a trend of lower concentrations of TP in more acidic lakes.

Zooplankton

Zooplankton community structure in the 20 study lakes was analyzed based on the number of species, abundance of individuals, and the distribution of individuals among the various species. In addition, two common multivariate statistical techniques were used to reduce the dimensionality of the data and to generate trends from the complicated data base. The first method involved classification of the zooplankton communities in the 20 study lakes based on cluster analysis and a calculated similarity matrix. The second method involved ordination, i.e. extraction of principal coordinates for the 20 lakes from the multidimensional hyperspace based on their zooplankton communities. These statistical methods show correlations between environmental factors and biotic responses but do not imply causation. If similar trends are depicted by each technique, a stronger correlation between pH and zooplankton communities can be deduced.

1. Community Structure.

Reduced species richness is often associated with acid-stressed environments. As the number of species decreases, the rare species are lost, and

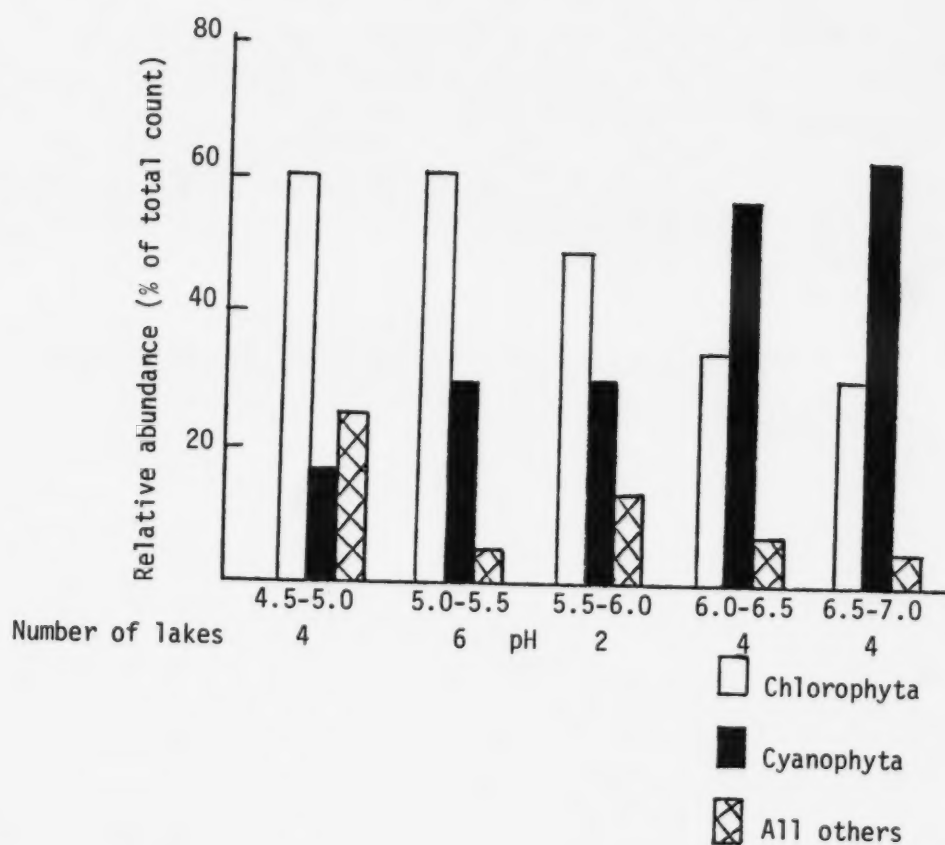


Figure 6-11. Relative abundance of major phytoplankton taxa in the lakes grouped within five pH intervals.

TABLE 6-6. Phytoplankton distribution with pH from 20 Florida study lakes.

Phytoplankton	4.5-5.0	5.0-5.50	5.51-6.0	6.01-6.5	6.51-6.7
<i>Staurastrum</i> sp.	X				
<i>Scenedesmus</i> sp.	X		X		X
<i>Lyngbya</i> sp.	X			X	
<i>Oscillatoria limnetica</i>	X	X	X	X	X
<i>Peridinium inoenseptatum</i>	X	X		X	X
<i>Chromonas</i> sp.	X	X	X	X	X
<i>Ankistrodesmus falcatus</i>	X	X	X	X	X
<i>Selenastrum minutum</i>	X	X	X	X	X
<i>Chlamydomonas</i> sp.	X	X	X	X	X
<i>Elakatothrix gelatinosa</i>				X	
<i>Rhabdoderma</i> sp.		X	X	X	X
<i>Anacystis incerta</i>	X	X	X	X	X
<i>Gloetheca linearis</i>	X	X			X
Pennate diatom sp.	X	X			X
<i>Tabellaria</i> sp.	X		X	X	X
<i>Closterium</i> sp.	X	X		X	X
<i>Euglena</i> sp.	X	X	X	X	X
Small green coccoids	X	X	X	X	X
<i>Oocystis pusilla</i>	X	X	X	X	X
<i>Dinobryon</i> sp.	X		X	X	X
<i>Anacystis montana</i>		X	X	X	X
<i>Phacus</i> sp.		X	X	X	
<i>Cosmarium</i> sp.		X	X	X	
<i>Tetraedon minimus</i>		X	X	X	X
<i>Chroococcus limneticus</i>			X	X	X
<i>Synedra</i> sp.		X	X	X	X
<i>Kirchneriella contorta</i>		X	X	X	X
Unknown green species		X	X	X	X
<i>Closteriopsis</i> sp.		X	X	X	X
<i>Dactylococopsis raphidioides</i>		X			
<i>Crucigenia tetrapedia</i>		X	X		X
<i>Microcystis aeruginosa</i>		X		X	
<i>Chlorella</i> sp.		X	X	X	X
Centric diatom sp.		X	X		
<i>Gomphosphaeria lacustris</i>		X	X	X	X
<i>Pseudotetraspora</i> sp.		X			
<i>Gonyostomum semen</i>			X	X	
<i>Spirulina laxissima</i>			X		
<i>Aphanothece nidulans</i>			X		X
<i>Asterionella formosa</i>			X		X
<i>Anabaena</i> sp.			X	X	X
<i>Melosira hernogii</i>			X	X	X
<i>Rhizosolenia</i> sp.			X	X	X
<i>Chlorogonium elongatum</i>			X		
<i>Oscillatoria angustissima</i>				X	
<i>Anacystis</i> sp.				X	X
<i>Echinosphaerella</i> sp.				X	X
<i>Gleocapsa rupestris</i>				X	
<i>Staurodesmus</i> sp.				X	
<i>Schizothrix calicicola</i>					X
<i>Mallomonas</i> sp.				X	X

species that can tolerate the altered environmental conditions increase in dominance. Increased acidity in freshwater systems has been associated with a general decrease in the number of zooplankton species (Yan 1979; Sprules 1975; Parsons 1968). In the present study, the mean number of zooplankton species in the nonacidic group was 19, while in the acidic group only 14 species were found (Table 6-7). The Kruskal-Wallis rank-sum test indicated that the number of zooplankton species in the various lakes was statistically different at $\alpha = 0.005$. The distribution of species richness across 5 pH intervals (Figure 6-12b) showed a monotonic increase in the number of species from the second lowest pH interval (13.5 species at pH 5.0 - 5.5) to the highest interval (19.5 species at pH 6.5 - 7.0). The most acidic group (pH 4.5 - 5.0) had approximately the same number of species (13.7) as the next pH interval. The range of species richness was relatively small over the entire pH spectrum, suggesting that pH does not have an overwhelming effect on zooplankton diversity in Florida lakes.

The number of zooplankton species found in the present study is much higher than the numbers reported in other studies on lakes of comparable pH. In a study of acidic lakes near Sudbury, Ontario, Yan (1979) found about half as many zooplankton species in lakes with pH values comparable to the acidic Florida lakes. Leivestad et al. (1976) found that numbers of zooplankton species in acidic Norwegian lakes were a third to a half of those observed in the present study. Lower concentrations of toxic heavy metals that are often associated with acid precipitation may be responsible for the higher species diversity found in Florida lakes, but further studies are necessary to evaluate this hypothesis. In addition, subtropical lakes in Florida are not subjected to the harsh seasonal fluctuations that occur in temperate lakes. The range of temperature in the Florida lakes was about 12 to 30°C during the year of sample collection. All 20 lakes are oligotrophic or mesotrophic, and none exhibited anoxic conditions in the water column. With such moderate environmental conditions, the adaptive potential of organisms to an external stress such as increased acidity may be enhanced.

The population density of zooplankton also has been shown to decrease with decreasing pH (Yan 1979; Yamamoto 1972; Parsons 1968). The mean abundance of zooplankton in the 10 acidic Florida lakes (Table 6-7) was 7.5×10^4 individuals/m³ (range 3.0 - 13.8×10^4), while the corresponding values for the 10 nonacidic lakes were 14.5×10^4 and 3.8 - 32.6×10^4 . The scatter in population values at a given pH precludes delineation of a simple trend between zooplankton population density and pH (Figure 6-12a), but the Kruskal-Wallis rank-sum test indicated significant differences ($\alpha = 0.005$) between the mean number of individuals in the lakes. Although a histogram of mean zooplankton numbers for the five pH intervals suggests a trend of increasing numbers with increasing pH, large and overlapping error bars were found for each interval.

The abundance of zooplankton in the lakes was influenced by phytoplankton density, as shown by the correlation between zooplankton numbers and chlorophyll levels in Figure 6-13. Since chlorophyll levels increased with increasing pH, the modest trend noted between zooplankton abundance and pH may reflect changes in overall lake productivity rather than direct effects of pH on zooplankton growth and survival rates.

Table 6-7. Summary data on zooplankton and related diversity indices in the 20 Florida lakes.¹

Lake	pH	Number of species	Individuals #/m ³	Biomass mg/m ³	Shannon- Weaver Index (H')	Evenness (H'/H _{max})	Modified Simpson's Index (SI*)
McCloud	4.71	11	79,400	116	0.86	0.77	0.82
Cowpen	4.84	13	30,500	24	0.86	0.73	0.82
Anderson-Cue	4.89	14	135,500	170	0.87	0.70	0.82
Galilee	4.96	17	86,400	110	0.99	0.76	0.87
Brooklyn	5.01	12	137,800	120	0.85	0.72	0.81
Rosa	5.05	13	77,900	175	0.66	0.55	0.69
Sheeler	5.09	12	33,200	33	0.86	0.75	0.83
Magnolia	5.10	15	47,300	57	0.83	0.66	0.81
Lowery	5.19	15	45,400	60	0.95	0.77	0.86
Johnson	5.20	14	79,000	64	0.89	0.73	0.83
Annie	5.72	16	108,900	72	0.81	0.63	0.79
Altho	6.00	18	70,400	49	0.93	0.71	0.84
Josephine	6.07	20	326,400	268	0.97	0.71	0.85
Geneva	6.12	18	93,500	132	0.89	0.67	0.83
Letta	6.37	18	150,200	92	0.89	0.67	0.80
Placid	6.40	17	154,300	103	0.94	0.74	0.84
June	6.64	21	201,600	137	1.07	0.78	0.88
Francis	6.66	23	194,300	190	1.03	0.74	0.85
Kingsley	6.68	15	109,800	66	0.86	0.68	0.80
Clay	6.69	19	38,400	120	0.95	0.71	0.83

1. Counts and biomass are averages of four (quarterly) samples. Diversity indices are calculated from mean counts of the four sampling dates.

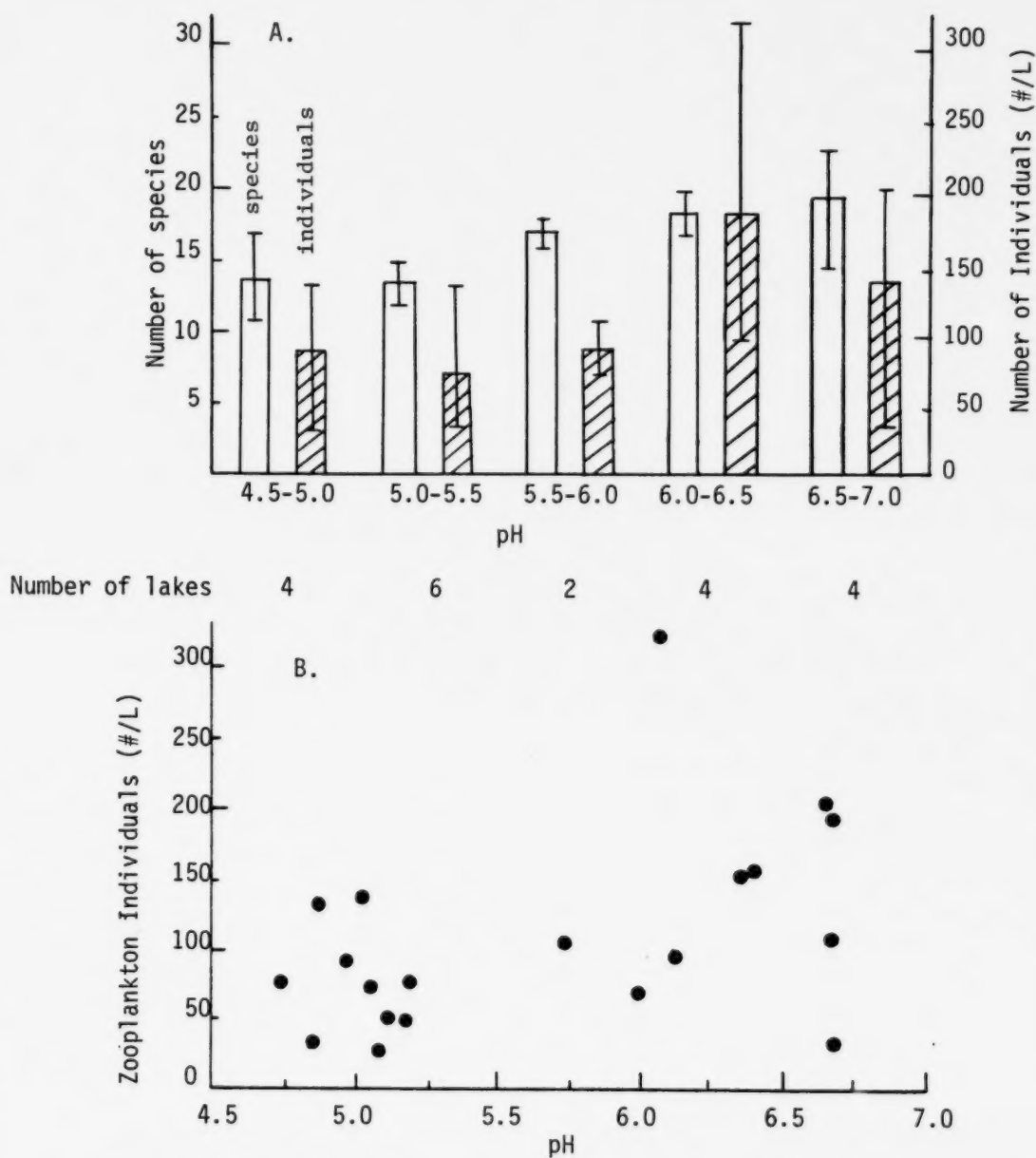


Figure 6-12. (A). Average number of species (per lake) and average number of zooplankton individuals per liter for the 20 lakes grouped into five pH intervals. (B). Average number of zooplankton individuals vs. pH in the 20 lakes.

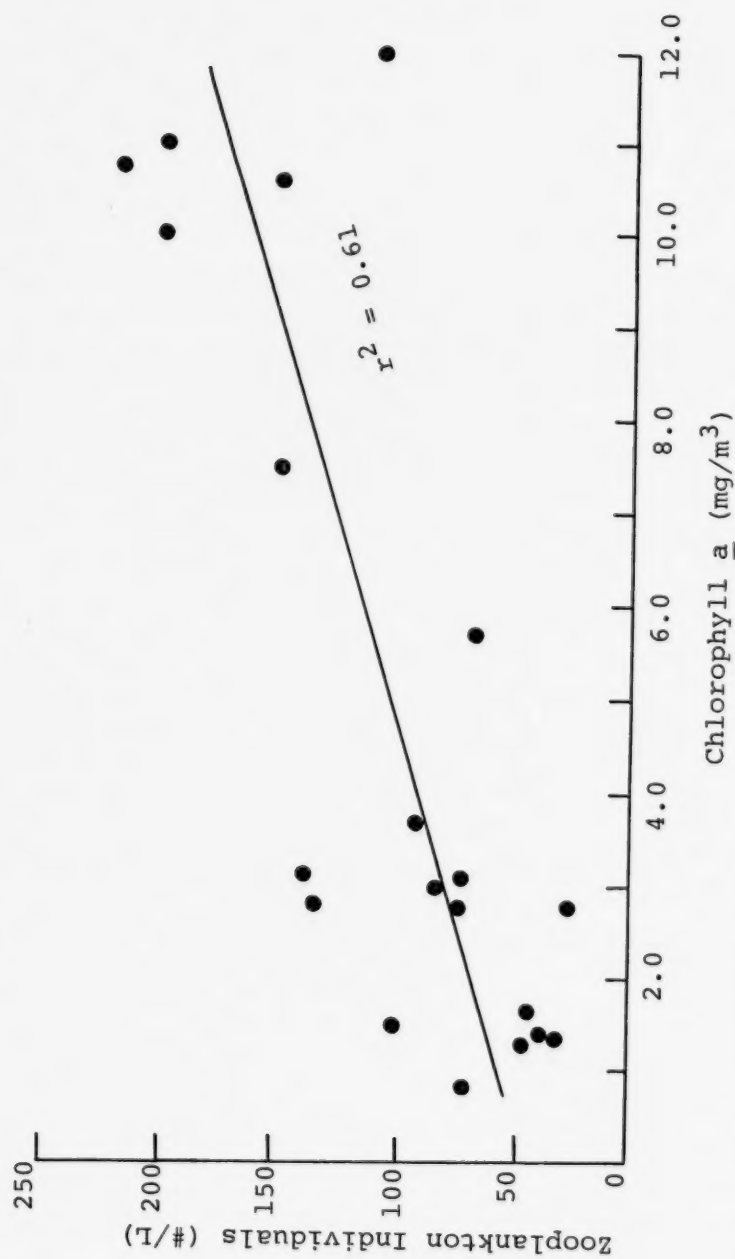


Figure 6-13. Relationship between zooplankton population density and chlorophyll a concentration in the 20 survey lakes. Data are averages for the four sampling dates.

Table 6-8. Composite species list from 50 Florida lakes over four quarters.¹

Organisms	Acid Lakes										Non-acid Lakes									
	pH 4.7					to					5.2					to				
	McCloud	Cowpen	Anderson	Galilee	Brooklyn	Rosa	Sheeler	Magnolia	Lowery	Johnson	Annie	Alto	Josephine	Geneva	Lotta	Placid	June	Francis	Kingsley	Clay
<u>Copepoda</u>																				
<i>Diaptomus floridanus</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Cyclops varicans</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Mesocyclops edax</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Tropocyclops prasinus</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Ergasilus</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Copepodite</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Nauplii</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<u>Cladocera</u>																				
<i>Bosmina longirostris</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Daphnia ambigua</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Diaphanosoma brachyurum</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Immature Cladocerans</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Chydorus sphaericus</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Bosminopsis dietersi</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Ceriodaphnia reticulata</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Simoccephalus</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Holopedium amazonicum</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<u>Rotifera</u>																				
<i>Keratella cochlearis</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Trichocerca multierinus</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Polyarthra vulgaris</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Trichocerca longiseta</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Conochilus unicornis</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Keratella taurocephala</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Kellicottia</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Brachionus quadridentata</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Brachionus havanaensis</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Filinia</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Monostyla</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Brachionus angularis</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Keratella quadrata</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Brachionus calyciflorus</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Pleusoma</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Gastropus</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Monommata</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Platyias patulus</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Conochiloides</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Lecane</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

¹Lakes listed in order of increasing pH. X indicates the species was found in the lake at least once during the four quarters.

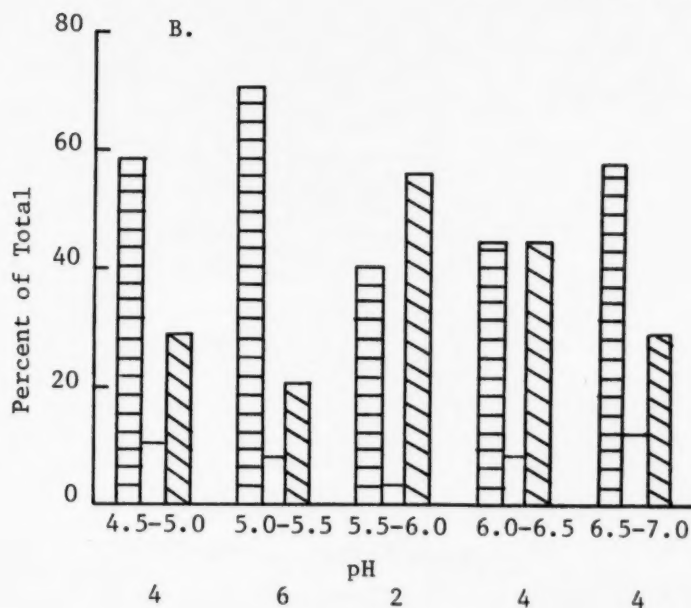
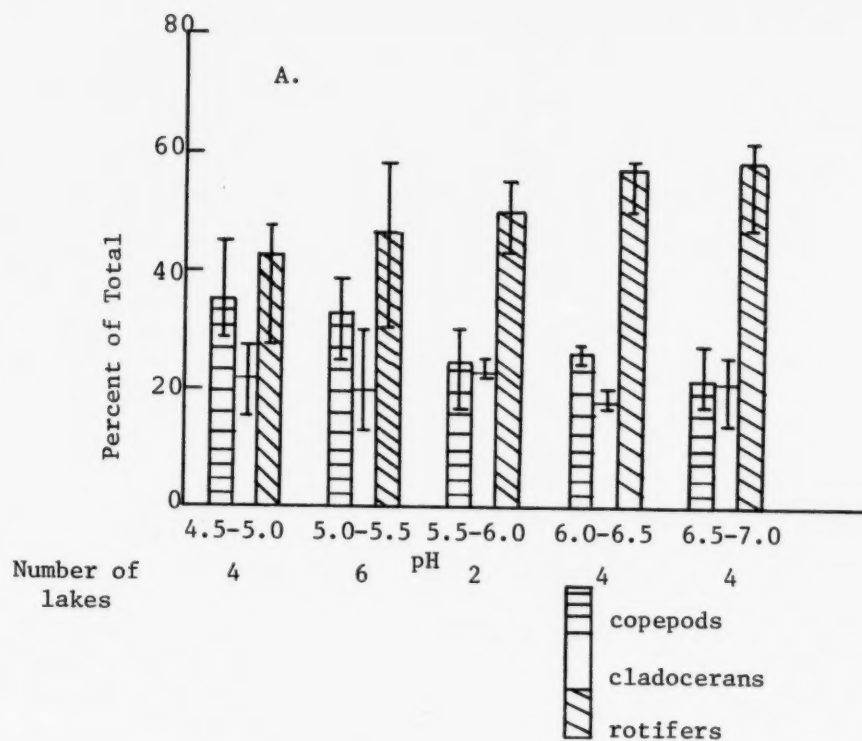


Figure 6-14. Average percent contributions of three major groups of zooplankton to total number of species (A) and individuals (B) for the 20 lakes grouped into five intervals.

group of lakes. Based on these results, no clear trends in the percent of total zooplankton abundance can be detected across the pH spectrum.

Species diversity indices have been widely used to describe biotic communities in ecological studies (Sanders 1968; Pielou 1969). In the present study, three diversity measures (Table 6-7) were calculated from the mean annual zooplankton data for the 20 lakes. Simpson's Index [$SI = \sum n_i(N_i - 1)/N(N - 1)$] defines the probability that two individuals selected at random will be of the same species (Simpson 1949). In the present study, we report $SI^* = 1.0 - SI$ so that values of 1 and 0 correspond to total evenness and extreme skew, respectively. In addition, both the Shannon-Weaver function [$H' = \sum P_i \log (1/P_i)$] and evenness [H'/H'_{max}] were computed.

The mean value of SI^* from the acidic lakes was 0.82, and the mean value from the nonacidic lakes was 0.83; thus based on this index, no differences in the zooplankton communities can be discerned between the acidic and nonacidic lakes. The mean value of H' for the acidic lakes was 0.89, and the mean value for the nonacidic lakes (0.93) reflects slightly greater species richness. The two groups of lakes had nearly identical evenness measures ($E = 0.71$ for the acidic lakes; $E = 0.70$ for the nonacidic lakes). Since H' has both an evenness and a species richness component, the higher H' for the nonacidic lake group thus reflects a higher number of species. Overall, the similar mean values for the three measures of diversity for the two groups of lakes indicates that little difference exists in the species diversity of the zooplankton communities of acidic and nonacidic Florida lakes.

2. Classification of Zooplankton Communities

Cluster analysis was used to identify patterns in the zooplankton communities associated with increased acidity. This method assumes that some general set of controlling factors is acting on the biotic community. Thus, the various species assemblages act as a natural bioassay, permitting the detection of major influences exerted by environmental and biological parameters. Conclusions drawn from this multivariate technique, as well as those from the univariate techniques used earlier in this section, are correlative and do not prove causation. Sneath and Sokal (1973) discussed the principles and techniques of classification in detail, while Poole (1974) has reviewed methods for cluster analysis. Czekanowski's similarity index was used to measure the similarity between the various zooplankton communities (Cormack 1971). Recent studies (Bloom 1979) have demonstrated the superiority of this index over other indices to accurately group assemblages of known similarity. The zooplankton data were log transformed ($X' = \ln(x + 1)$), and no standardization was used. Two types of classifications were generated: standard (Q-mode) analysis, which clusters the lakes according to the similarity of their species composition, and reverse (R-mode) analysis, which clusters the species according to their similarity of occurrence. Both analyses were performed using quantitative (actual count) data and qualitative (presence-absence) data. The former thus includes information on the relative dominance of species, while the latter disregards abundance.

Results of the cluster analyses are presented as dendrograms, in which

groups of similar objects are depicted by the joining of lines into progressively larger groups. The dendrogram generated from Q-mode quantitative classification of quarterly zooplankton data from the 20 lakes (Figure 6-15) shows a strong effect of seasonality on zooplankton communities; clusters of highest similarity level generally comprised of various lakes within a single season. At an arbitrarily defined similarity level of 63%, 11 groups of two or more stations were defined, along with a number of solitary stations. Clusters g, h, i, j and k are comprised primarily of acid lakes, and a single season (fall, winter, or spring) dominated each cluster. Two nonacidic lakes (Kingsley and Geneva) also are included in this group. Clusters b and e are mostly from summer samples and are made up of both acidic and nonacidic lakes. Clusters c, d and f are dominated by nonacidic lakes from all four seasons. The overall trend suggests that a greater difference in zooplankton communities exists between the acidic and nonacidic groups during fall, spring and winter and that a higher level of similarity exists during summer. Results of Q-mode classification based on presence-absence data followed the same patterns described for the quantitative data. The level of similarity of the various groups was higher because the effect of dominance was removed by considering only presence-absence data.

In order to assess the overall yearly trends in zooplankton communities, a classification was conducted on the yearly mean data. A dendrogram obtained from the mean annual quantitative data (Figure 6-16) shows that two major groups are formed at the 68% similarity level. One group is composed of seven lakes with a pH range of 6.00 to 6.69. The second group contains ten acidic lakes (mean pH 4.71 to 5.2) and three nonacidic lakes. The latter three lakes all are considerably more oligotrophic than the other nonacidic lakes, suggesting that the zooplankton communities are heavily influenced by phytoplankton abundance.

An R-mode cluster analysis using quantitative data on the species in the 20 lakes (Figure 6-17) shows that the group of dominant, acid-tolerant species grouped together at a high level of similarity. These six species, along with copepodites and nauplii, formed a group at the 87% similarity level. Species groups were added to this central group in order of decreasing occurrence and abundance.

3. Ordination of Zooplankton Communities

Ordination methods are useful in extracting information on underlying factors or trends from a complicated data base. Ordination techniques such as principal component analysis and factor analysis have been used in both terrestrial and aquatic studies (Bray and Curtis 1957; Shannon and Brezonik 1972). In the present study, principal coordinate analysis (PCOR) was applied to log-transformed data from the 20 study lakes, and a series of principal axes were calculated to account for the variance within the placement of the stations. The principal axes are linear combinations of the variables that explain the maximum possible variance in the original data. In simple terms, the principal axes can be considered as new (derived) variables that reduce the dimensionality of the original data set. The derived variables can be considered as underlying factors explaining the variations in the measured variables. For further explanations of ordination techniques, see Gower

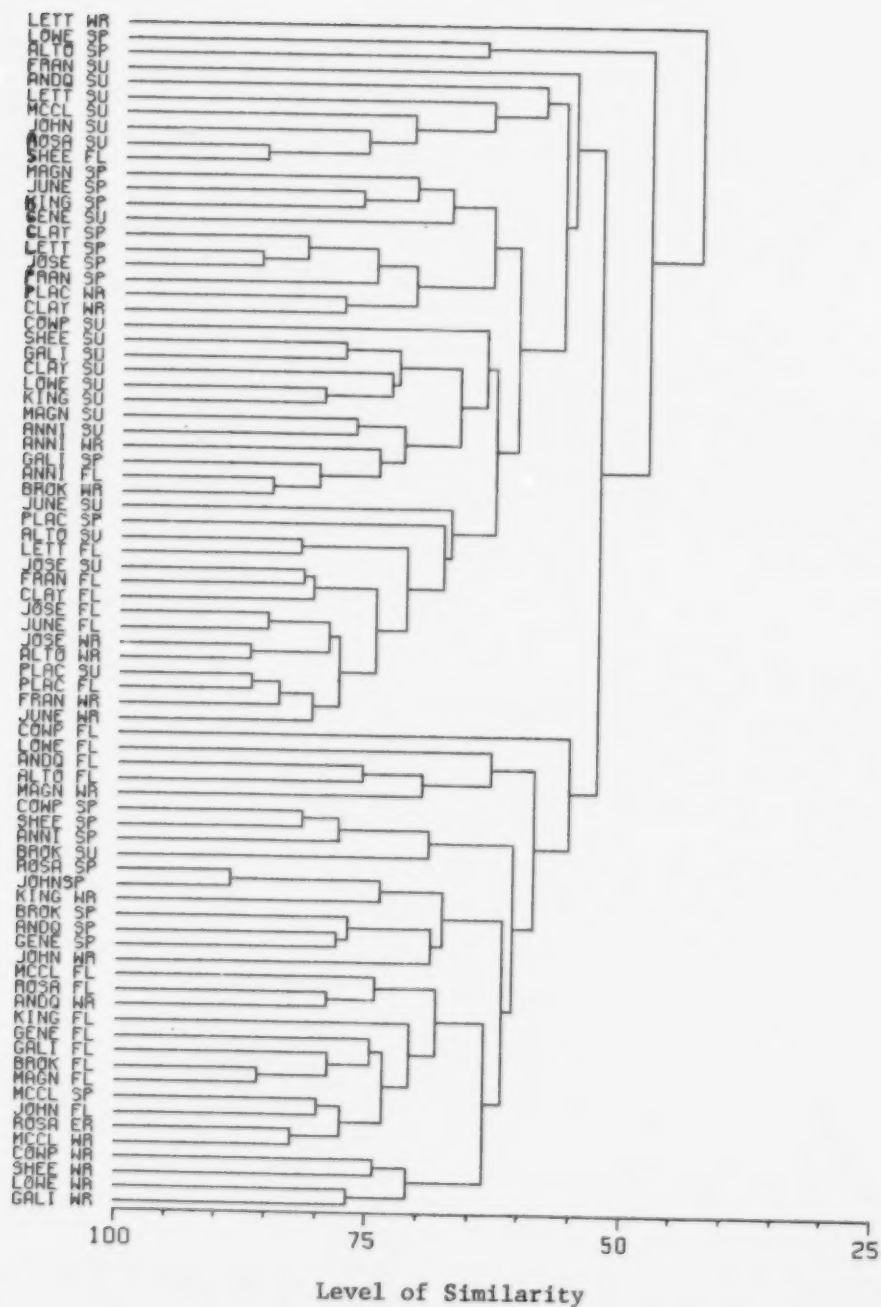
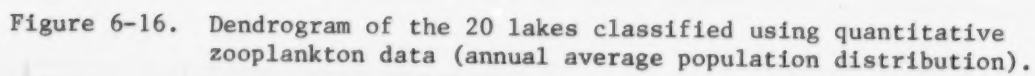


Figure 6-15. Dendrogram of the 20 lakes based on quarterly quantitative zooplankton data. Names on the left represent lakes and seasons sampled.



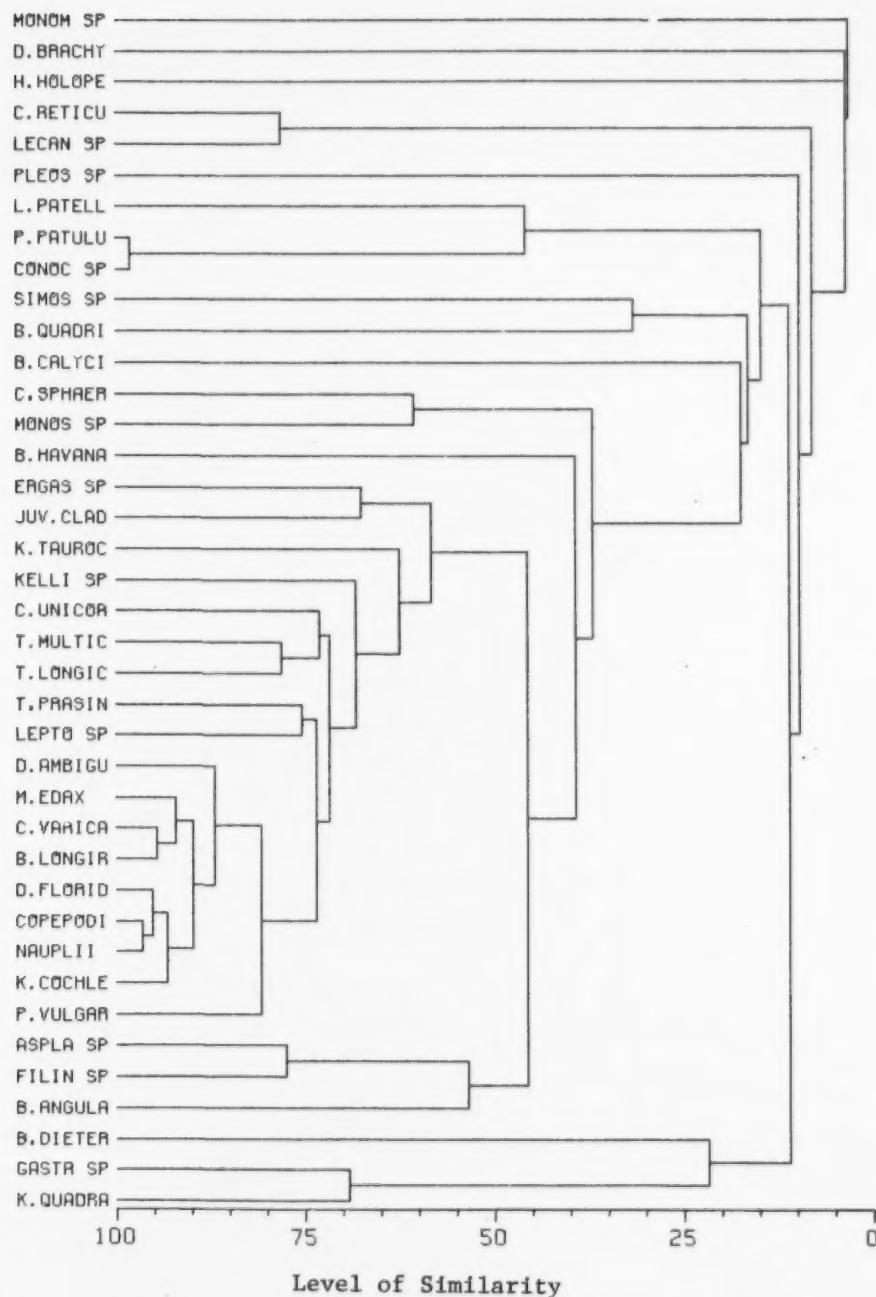


Figure 6-17. Dendrogram from an R-mode classification of zooplankton taxa, based on annual average population densities in the 20 lakes.

(1966), Sneath and Sokal (1973), and Poole (1974).

Principal coordinate analysis of the zooplankton data was done using a computer program described in Bloom et al. (1977). The zooplankton counts for each lake were first log-transformed (to obtain normal distributions), and Z-scores for each species were then computed so that all variables had means of zero and unit variance. Figure 6-18a presents a three dimensional view of the 20 lakes plotted on the first three principal axes. These axes account for 54% of the variance in the data, which is rather good for such a complicated data base. The overlap of several of the lakes in Figure 6-18a obscures some of the information, and the exact location of each lake on the three axes can be obtained from Figures 6-18b and c, which show cross-sectional views of the 20 lakes on planes representing axes I and II, and I and III, respectively.

Two main groups of lakes are visible from Figure 6-18b, a dense group of 13 lakes and dispersed group of 7 lakes. The latter group contains only nonacidic lakes, and the other group consists of ten acidic and three nonacidic lakes. These two groups of lakes agree in composition with the two groups obtained in the cluster dendrogram (Figure 6-16), further indicating a difference in the zooplankton communities of the two groups of lakes. Within the group of seven nonacidic lakes, three lakes (Josephine, Francis and June), are located away from the rest of the group, and they had the highest numbers of individuals and the greatest number of species of all 20 lakes. A further similarity between the clustering and ordination results is in the relative positions of Lake Cowpen and Lake Sheeler. Both lakes are highly acidic with low-color content, and both had reduced species richness and low zooplankton abundance. These lakes were the last to be added to the cluster of acid lakes (Figure 6-16), and both are grouped together (and at some distance from the other acidic lakes) in the ordination graphs (Figure 6-18a-c).

The overall pattern depicted by the multivariate analyses suggests that a difference exists between acidic and nonacidic lakes, but low productivity nonacid lakes are grouped with the acid lakes.

Benthic Invertebrates

Community structure of the benthic invertebrate assemblages from the 20 study lakes was analyzed based on species richness, abundance of individuals and species diversity. In addition, both cluster analysis and ordination were used to detect differences in the structure of the benthic communities among the 20 study lakes.

1. Species Richness

Reductions in the number of benthic species have been related to increases in acidity in lakes (Parsons 1968; Leivestad et al. 1976). The present data also indicate a slight reduction in the mean number of benthic species with increasing acidity (Table 6-9). The mean number of species in the 10 acidic lakes ($\text{pH} < 5.6$) was 24.6 (range of 21 to 30), and the mean number in the 10 nonacidic lakes ($\text{pH} > 5.6$) was 26.6 (range 17 to 37). The mean numbers of benthic species within the 20 lakes was found to be statis-

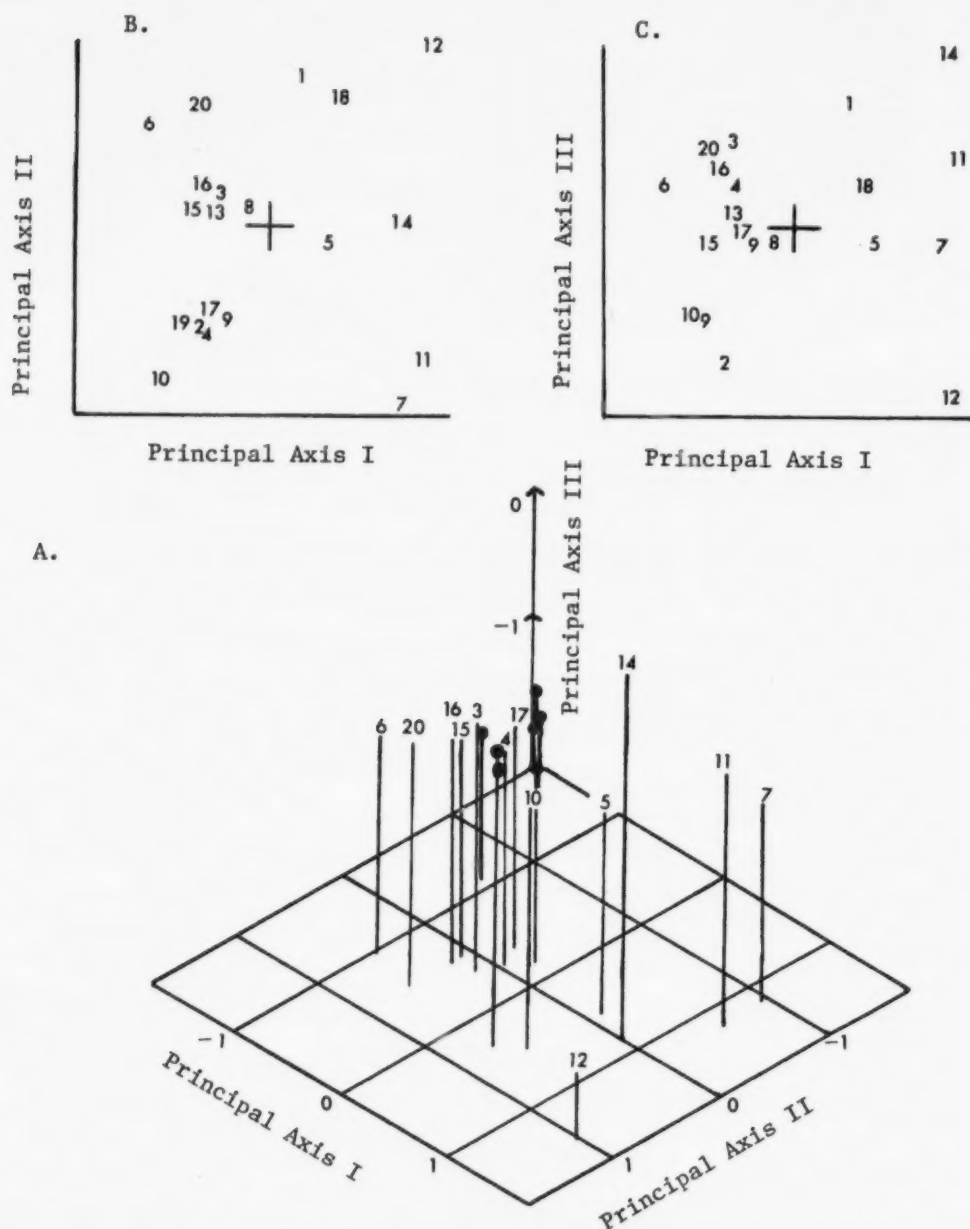


Figure 6-18. Principal coordinate analysis of study lakes based on zooplankton community structure. A. Placement of lakes on first three principal axes. B and C. Placement of lakes on the first and second and first and third principal axes, respectively. For lake number code see Table 6-1. Black circles represent overlapping lakes.

Table 6-9. Summary of data on benthic invertebrates and related diversity indices for 20 Florida lakes.¹

	pH	Number of Species	Individuals (#/m ²)	Biomass (g/m ²)	Shannon- Weaver Index (H')	Modified Simpson Index (S*)	Evenness Index (H' / H' max)
McCloud	4.71	28	5380	0.354	0.88	0.81	0.61
Cowpen	4.84	30	2130	0.168	1.05	0.85	0.71
Anderson-Cue	4.89	25	3720	0.364	0.85	0.75	0.61
Galilee	4.96	24	1450	0.403	1.06	0.88	0.77
Brooklyn	5.01	26	1100	0.320	1.14	0.81	0.90
Rosa	5.05	23	3990	0.376	0.87	0.80	0.64
Sheeler	5.09	23	2950	0.428	0.75	0.73	0.55
Magnolia	5.10	21	2590	0.557	0.75	0.76	0.57
Lowery	5.19	23	940	0.223	1.03	0.86	0.76
Johnson	5.20	23	980	0.335	1.02	0.85	0.75
Annie	5.72	17	2860	0.299	0.59	0.60	0.48
Altho	6.00	17	1240	0.080	0.69	0.68	0.56
Josephine	6.07	33	2130	0.596	1.85	0.56	0.71
Geneva	6.12	24	690	0.127	1.05	0.86	0.76
Letta	6.37	25	1220	0.331	1.12	0.90	0.80
Placid	6.40	27	1940	0.728	1.04	0.86	0.73
June	6.64	37	2330	0.705	1.05	0.84	0.67
Francis	6.66	32	2490	0.632	0.99	0.86	0.66
Kingsley	6.68	22	1980	0.254	0.83	0.77	0.62
Clay	6.69	32	3960	0.457	0.80	0.53	0.73

¹Values are averages for the four sampling periods.

tically different using a Kruskal-Wallis test ($\alpha = .005$). The mean number of species showed considerable variation between lakes in both the acidic and nonacidic groups. The nonacidic group of lakes exhibited the greatest variability, a fact that can be attributed to the greater trophic diversity of this group. Lakes with the highest numbers of species routinely were the most productive. Arranged according to the five previously established pH intervals, a bimodal pattern of species richness emerged with the greatest number of species occurring in lakes of either the highest or lowest pH (Figure 6-19). Such a distribution suggests that species richness in the study lakes is controlled by factors other than pH.

The importance of sediment characteristics as controlling factors for benthic community structure has been well-established (Harp and Campbell 1967; Bloom et al. 1972). The wide variation in species richness at all pH levels in this study may in part be attributed to interlake variations in sediment characteristics. Based on the previously established productivity - pH relationship, organic deposition and thus sediment organic content may be expected to decrease with decreasing pH. Thus, species requiring a highly organic substrate for deposit feeding or burrow formation may be excluded from lower pH lakes. The variation in benthic response within a given pH interval is a reflection of the fact that the organic content of sediments is influenced by allochthonous organic inputs from the watershed, as well as autochthonous production. Both the quality and quantity of food may limit benthos distribution. Filter-feeding species may be eliminated from low pH lakes due to the generally lower algal concentrations in these lakes. In addition, bacteria, which are an important dietary component for some benthic invertebrates, are in reduced concentrations in acidic habitats (Anderson et al. 1978).

2. Number of Individuals

A reduction in the total number of benthic individuals has been associated with increased acidity (Lackey 1938; Harp and Campbell 1967). Results from the present study (Table 6-9) indicate a high degree of variability among the 20 study lakes, with no clear reduction in the abundance of benthic invertebrates associated with increased acidity. The mean number of benthic invertebrates in the 10 acidic lakes ($\text{pH} < 5.6$) was $2,520/\text{m}^2$, with a range of 936 to $5,380/\text{m}^2$; and nonacidic group ($\text{pH} > 5.6$) had a mean of $2,080/\text{m}^2$, with a range of 692 to $3,960/\text{m}^2$.

When grouped into five pH-intervals, the abundance data display a bimodal pattern, with the most acidic lakes and the least acidic lakes containing the greatest number of individuals (Figure 6-19). The results demonstrate a decline in abundance in moderately acidic lakes ($\text{pH} 5.5 - 6.0$), but they do not delineate a consistent reduction in benthic invertebrates with decreasing pH.

Larvae of the dipteran, Chaoborus punctipennis, were often collected in benthic samples and were counted as part of the benthic invertebrate assemblage in the present study. C. punctipennis is associated with bottom sediments during the day and migrates up through the water column at night (Roth 1968). Elimination of this species from the benthic counts decreased the total number of individuals at all pH levels but failed to change the general abundance-pH relationship discussed above.

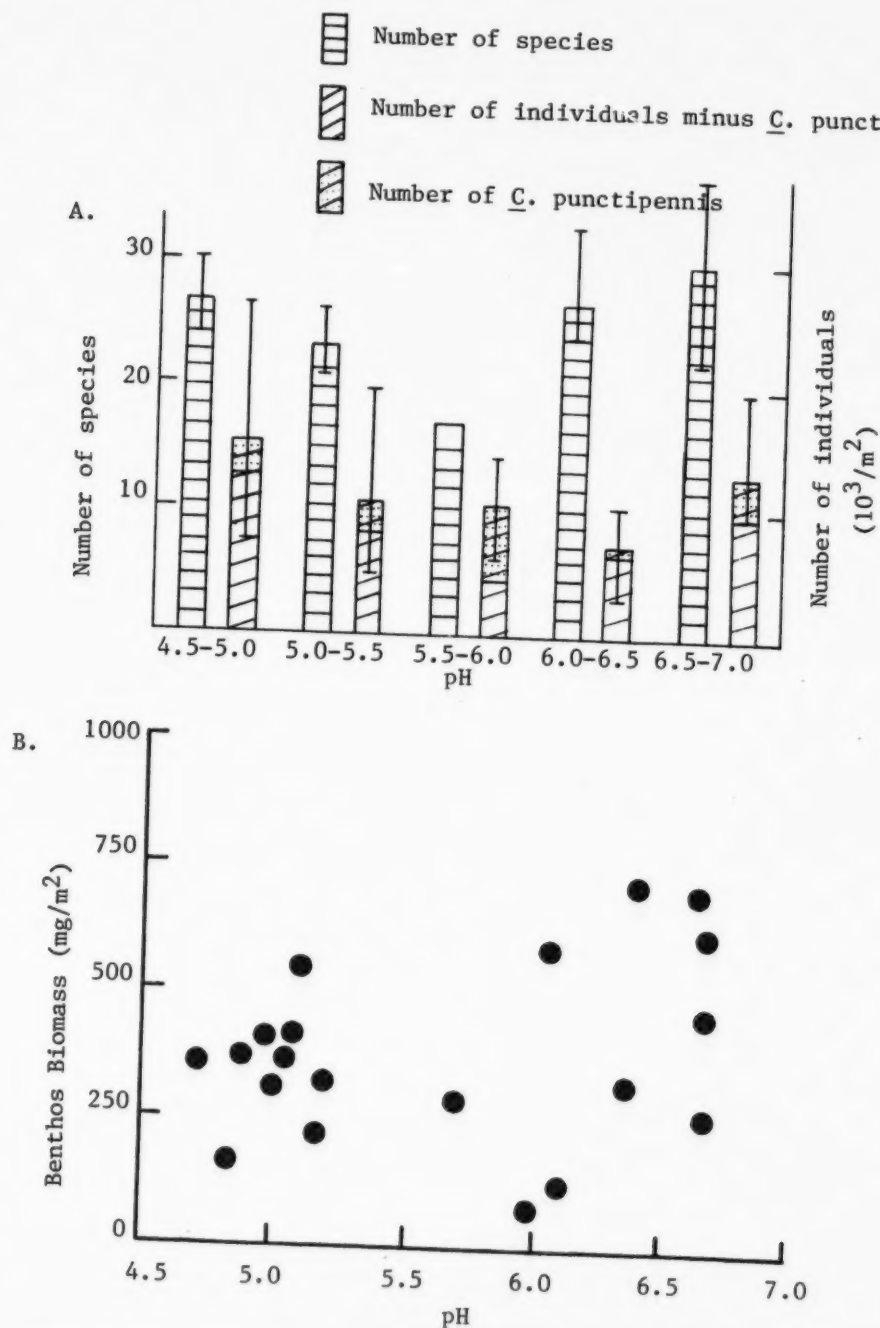


Figure 6-19. (A). Mean number of species of benthic invertebrates and their mean population density for the 20 lakes grouped into five pH intervals. (B). Mean areal biomass of benthos (ash-free dry weight) vs. pH in the 20 survey lakes.

3. Biomass of Benthic Invertebrates

Biomass of benthic invertebrates (ash-free dry weight) generally decreased with decreasing pH in the 20 Florida lakes (Table 6-9). Mean biomass for the 10 acidic lakes was 0.32 g/m^2 and for the 10 nonacidic lakes was 0.42 g/m^2 . The large variation in biomass of benthic invertebrates in the lakes (Figure 6-19) suggests that additional factors besides pH influence the distribution of the benthos.

4. Species Diversity

Species diversity was calculated separately for each of the 20 lakes as Shannon-Weaver (H'), evenness, and Simpson (SI^*) indices. The 10 acidic lakes had a mean value for $\log H'$ of 0.94 and a range of 0.75 to 1.44, but the 10 nonacidic lakes had a slightly lower mean value of 0.90 and a range of 0.59 to 1.12 (Table 6-9). Thus, no clear relationship between Shannon-Weaver diversity and pH could be delineated.

Mean values for the modified Simpson's index (Table 6-9) were 0.82 (acidic lakes) and 0.86 (nonacidic lakes). Simpson's index is sensitive to dominance by a few species. The slightly higher value for SI^* from the 10 nonacidic lakes reflects a more even distribution of individuals among the various species. Overall, very little difference exists between the two lake groups in reference to the three measures of diversity, and no strong relationship could be established between these indices and pH.

5. Community Composition

The relationship of individual species or groups of species to pH can provide useful data on the response of benthos to acidification. A group of nine acid-tolerant species dominated invertebrate assemblages at all pH levels: Limnodrilus hoffmeisteri, Hyalella azteca, Bezzia sp., Chaoborus punctipennis, Coelotanytus tricolor, Procladius sp., Stictochironomus devinctus, Cladotanytus sp., and Tanytarsus sp. Other species also occurred at all pH levels but were never present in large numbers (Table 6-10). Chironomid larvae were an important component in the benthic communities of all the lakes and accounted for nearly 50% of the number of individuals, as well as a majority of the species in the acidic lakes. Chironomids were found in all nonacidic lakes but accounted for a smaller portion of the individuals and species richness than in the acidic lakes. A replacement series of major invertebrate groups was noted along the pH gradient (Figure 6-20). Oligochaetes and amphipods increased in importance with increasing pH, but chironomids and molluscs decreased with increasing pH. No individuals of the latter group were found in lakes of $\text{pH} < 6.0$.

Decapods such as Palaemonetes paludosus were found only in lakes with high pH. In most cases, species restricted to nonacidic lakes were found in low numbers when present. Similarly, several rare taxa were found only in acidic lakes: Macromia sp., Psychomyia sp., Zavrelia sp. and Pseudodiamesa pertnax.

Table 6-10. Composite species list of benthic invertebrates from 20 Florida lakes.
Lakes listed in order of increasing pH.

Organism	McCloud	Cowpen	Anderson-Cue	Galilee	Brooklyn	Rosa	Sheelar	Magnolia	Lowery	Johnson	Annie	Alto	Josephine	Geneva	Lotta	Placid	June	Francis	Kingsley	Clay
<i>Dugesia tigrina</i>					X								X			X	X	X	X	X
<i>Limnodrilus hoffmeisteri</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Lumbriculus</i> sp.	X		X	X			X	X	X	X	X		X	X	X	X	X	X	X	X
<i>Helobdella</i> sp.							X					X	X			X	X	X	X	X
<i>Illinobdella</i> sp.												X	X							
<i>Pisidium</i> sp.												X	X				X	X		
<i>Corbicula fluminea</i>															X		X	X		
<i>Eupera</i> sp.																	X	X		
<i>Pilea</i> sp.																	X	X		
Unid. Plecoptera													X				X			X
<i>Anadonotides</i> sp.																		X		X
<i>Rhyssa</i> sp.																	X	X		
<i>Amnicola limosa</i>																	X	X		
<i>Gyraulus deflectus</i>																	X	X		
<i>Viviparus intertextus</i>																	X			
<i>Hyalella azteca</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Crangonyx</i> sp.					X				X				X							
<i>Gammarus</i> sp.													X							
<i>Palaemonetes paludosus</i>																	X			
<i>Limnocythere</i> sp.																	X			
<i>Hexagenia</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Gomphus williamsi</i>	X				X					X				X						X
<i>Didymops</i> sp.													X							X
<i>Hagenius bevisstylus</i>								X												
<i>Celithemis</i> sp.	X												X							
<i>Macromia</i> sp.	X																			
<i>Sympetrum</i> sp.																				X
<i>Leptocella</i> sp.	X	X	X	X	X		X		X			X			X	X	X	X		
<i>Psychomyia</i> sp.				X																
Unid. Trichoptera			X		X				X					X	X		X	X		X
<i>Oxyethira</i> sp.		X			X															
Hydroptilidae	X	X				X		X					X					X		
<i>Bezzia</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Chaoborus punctipennis</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Procladius</i> sp.	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Tanytus</i> sp.																				X
<i>Ablabesmyia parajanta</i>	X	X	X	X	X	X	X	X	X	X			X	X	X	X	X	X	X	X
<i>Coelotanypus tricolor</i>	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X
<i>Coelotanypus scapularia</i>																				X
<i>Anatopynia</i> sp.		X			X		X				X		X							
<i>Paralauterborniella</i> sp.	X		X	X	X	X		X	X	X			X			X		X		
<i>Chironomus attenuatus</i>											X		X			X	X	X	X	X
<i>Cryptochironomus fulvus</i>		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Harnischia viridulus</i>	X	X	X	X	X	X	X	X	X	X	X		X	X	X		X		X	X
<i>Parachironomus pectinatella</i>	X	X	X	X		X	X					X	X						X	X
<i>Polypedilum halterale</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Polypedilum scalaenum</i>													X	X			X			

Table 6-10. Continued

<i>Glyptotendipes senilis</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Stictochironomus devinctus</i>	X	X	X	X	X		X	X	X	X	X		X	X	X	X	X	X	X
<i>Dicortendipes leucoscelis</i>		X	X	X			X		X	X			X		X	X	X	X	X
<i>Pseudochironomus sp.</i>	X	X	X	X	X	X	X	X	X				X		X	X	X	X	X
<i>Pentaneura sp.</i>	X														X	X		X	X
<i>Einfeldia sp.</i>														X					
<i>Paracladopelma sp.</i>							X		X							X			X
<i>Cladotanytarsus sp.</i>																X		X	
<i>Tanytarsus sp.</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Constempellina sp.</i>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
<i>Zavrelia sp.</i>			X																
<i>Milotanypus sp.</i>	X	X																	
<i>Psectrocladius sp.</i>	X	X																	
<i>Paratendipes sp.</i>								X					X		X				
<i>Orthocladinae</i>																X			
<i>Chironomidae pupa</i>													X		X			X	
<i>Psectrotanypus sp.</i>	X	X	X	X	X	X		X	X	X	X		X	X	X	X	X	X	X
<i>Pseudodiamesa sp.</i>		X				X				X									
<i>Trichocladius sp.</i>																			
<i>Cricotopus sp.</i>								X											
<i>Smittia sp.</i>						X	X												X
<i>Galerucella sp.</i>		X													X				
<i>Cylloepes sp.</i>	X	X	X			X	X								X				
<i>Bidessus sp.</i>			X			X									X			X	

In summary, the benthic assemblages of all 20 lakes were dominated by a group of species whose distribution appeared to be independent of pH. Individual species confined to either acidic or nonacidic lakes never constituted a major component of the benthos in any lake. Thus, changes in the partitioning of individuals among species rather than wholesale replacement of species was the principal response of benthic invertebrates to increasing acidification.

6. Classification of Benthic Communities

Benthic data were classified by standard (Q-mode) analysis using Czekanowski's Similarity Index on log-transformed quantitative data from the 20 study lakes. A Q-mode classification of quarterly quantitative benthic data (Figure 6-21) did not demonstrate the same high degree of seasonality displayed by the zooplankton data. The majority of lakes, both acidic and nonacidic, showed a stronger inter-lake similarity than intra-lake similarity when considering all four seasons of data. Two major groups can be identified from the Q-mode analysis (Figure 6-21); group A is composed of nonacidic lakes, and group B is composed principally of acidic lakes. The remainder of the dendrogram consists of a large number of very small clusters of both acidic and nonacidic lakes linked to groups A and B at decreasing levels of similarity. Such a loose pattern of association suggests that the structure of the benthic community is controlled less by pH than by additional factors, including substrate heterogeneity.

Classification of the 20 study lakes using a Q-mode analysis of quantitative benthic data expressed as a yearly mean for each lakes (Figure 6-22) identified two distinct clusters, one composed of acidic lakes (A) and one composed of nonacidic lakes (B). Six lakes, two acidic and four nonacidic, did not cluster within either group A or B. Two of the six lakes, Annie and Sheeler, are very oligotrophic and considerably deeper than the other study lakes.

7. Ordination of Benthic Invertebrate Data

Principal coordinate analysis based on Gower's distance measure, unit variance standardization, and log-normalized data resulted in a central lake group, and a small number of lakes some distance away (Figure 6-23a). The three dimensional representation of the lakes plotted on the first three principal axes accounted for 37% of the variance in the data. Lakes Cowpen (6) and June-in-Winter (12) show a high degree of dissimilarity from the remaining 18 lakes. Lake Cowpen (mean pH 4.84) contained the highest aluminum concentrations of the 20 lakes (Figure 6-6). Tricopterans and two species of chironomids (Tanytarsus sp. and Pseudochironomus sp.) were higher in Cowpen than the other lakes, and Chaoborus punctipennis, a major dominant in both the acidic and nonacidic lakes, was totally absent. Lake June-in-Winter (mean pH 6.64) contained the greatest number of benthic species, as well as the most species and greatest abundance of molluscs.

The exact location of individual lakes in the central cluster of Figure 6-23a can not be defined because of the overlap of lakes. This problem is overcome by examining the position of individual lakes on axes two and three

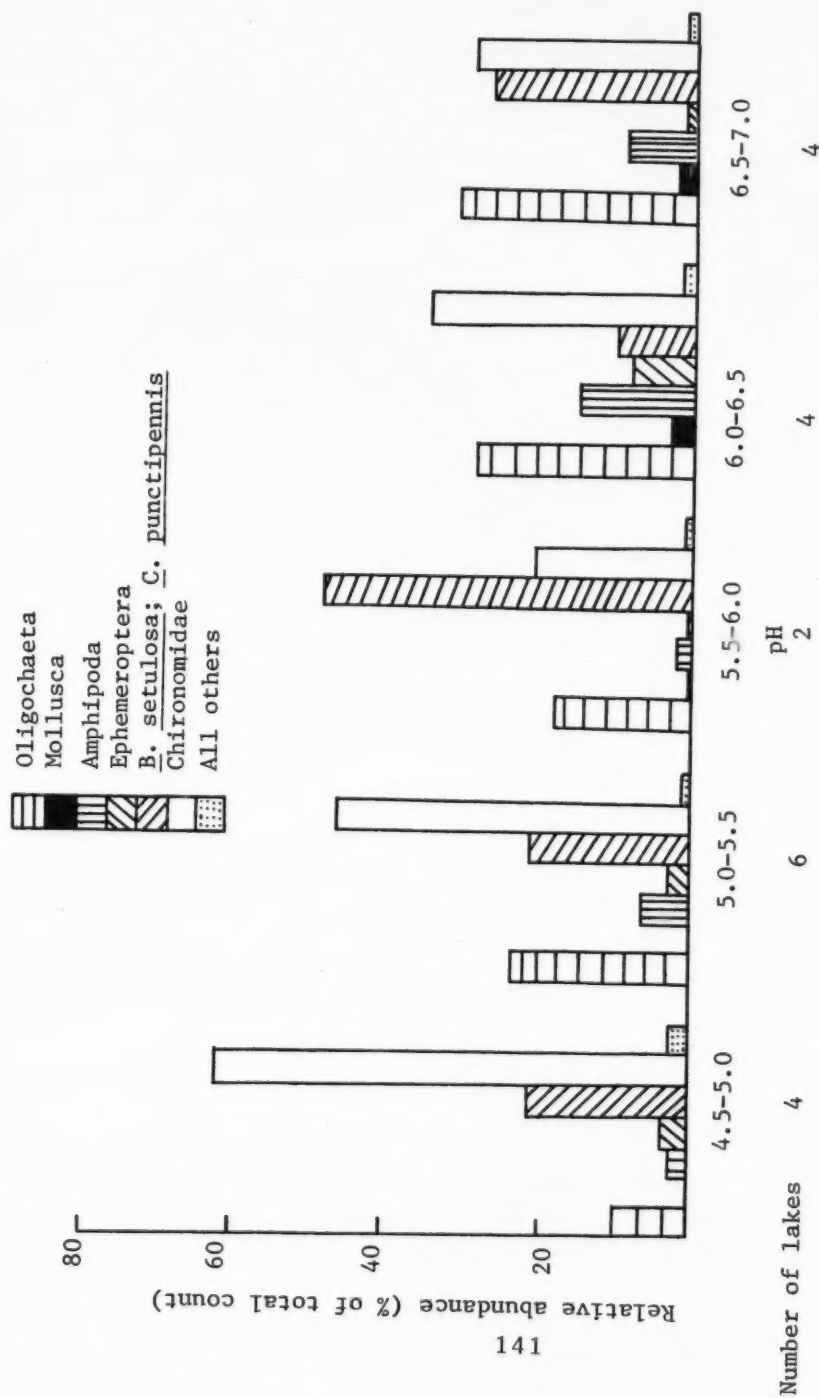


Figure 6-20. Percent contribution of selected groups of benthic invertebrates to the total number of benthic individuals in five pH intervals from 20 Florida lakes.



Figure 6-21. Dendrogram of the 20 lakes based on quantitative data for benthos. Names on the left represent lakes and season. NA is a nonacidic lake group; AC is an acidic lake group.

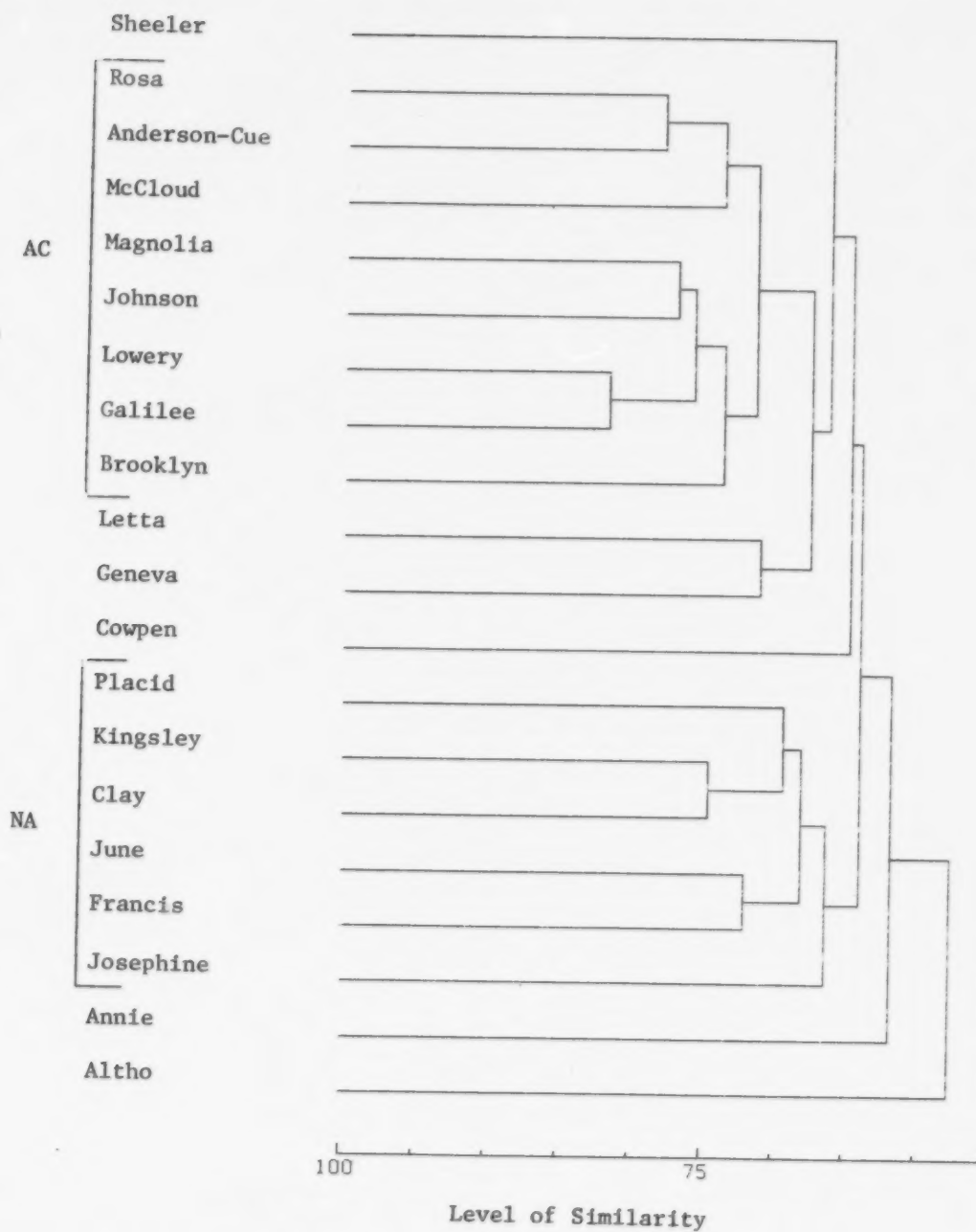


Figure 6-22. Dendrogram of the 20 lakes classified on the basis of mean annual data for benthos populations. AC is an acid group; NA a nonacid group of lakes.

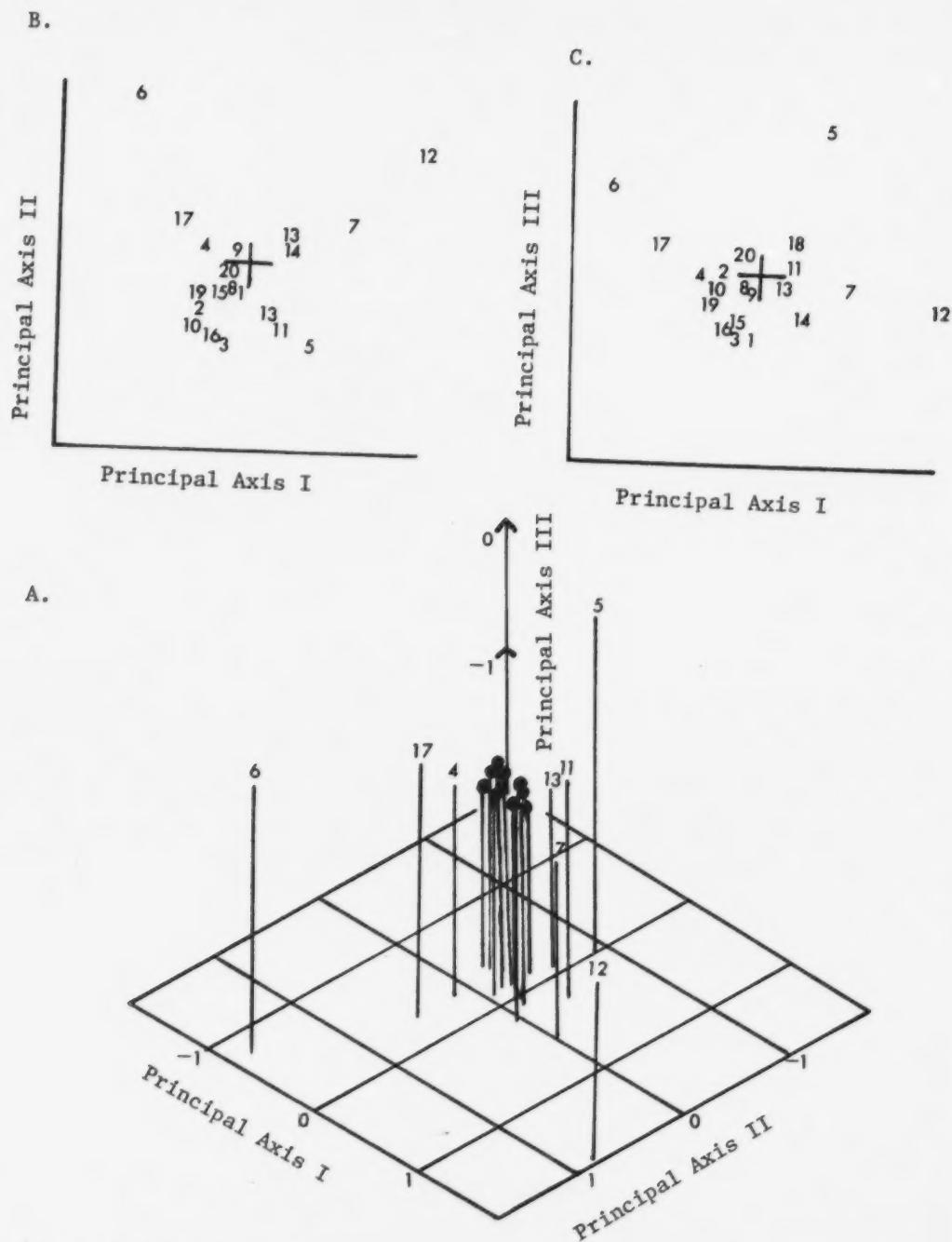


Figure 6-23. Principal coordinate analysis of study lakes based on benthic community structure. A. Placement of lakes on first 3 principal axes. B and C. Placement of lakes on first and second and first and third principal axes, respectively. For lake number code, see Table 6-1. Black circles represent overlapping lakes.

(Figures 6-23bc) relative to principal axis one. Two clusters are defined from a combination of the first and second principal axes (Figure 6-23b), one composed of six nonacidic lakes (cluster A) and one composed of nine acidic and three nonacidic lakes (cluster B). This arrangement suggests a correlation between the composition of benthic communities and pH. The inclusion of three lakes with high pH and relatively low productivity (i.e. Lake Geneva (14), Annie (11) Altho (12)) in the acidic cluster also suggests a correlation between trophic state and the structure of benthic communities.

The position of the 20 lakes on the first and third axes (Figure 6-23c) shows a high degree of similarity between the acidic and nonacidic cluster of lakes. No clear distinction is visible between the two groups of lakes with reference to their position along the third principal axis, suggesting that most of the variation in the benthic data that can be correlated with pH is explained along the first two principal axes.

In summary, both classification and ordination techniques demonstrated a general trend of greater similarity in the benthic communities of lakes with similar pH. These data do not indicate that a detrimental effect is being exerted by decreased pH on the benthic invertebrates.

Fish

Several preliminary studies on the fish populations in acidified Florida lakes also were undertaken as part of the present project. A qualitative survey of the fish fauna of Lake Sheeler (mean annual pH 5.09) was conducted with SCUBA during the summer of 1979. The narrow littoral zone was dominated by mosquito fish (Gambusia affinis) and secondarily by centrarchid fingerlings. The pelagic fauna, although somewhat sparse, was comprised of several species of centrarchids, including bream (Lepomis macrochirus) and largemouth bass (Micropterus salmoides), and one unidentified species of ictalurid catfish. Largemouth bass ranged in length from approximately 25 to 50 cm.

Adult largemouth bass were collected from McCloud Lake (mean annual pH 4.71) and Anderson-Cue Lake (mean annual pH 4.89) in July, 1979. A condition factor (K), relating body length (L, in mm) to body weight (W, in g) was calculated according to the formula:

$$K = \frac{105 W}{L^3}$$

(Nikolsky 1963). Fish body weight per unit body length (and thus the condition factor, K) should increase in response to enhanced growth conditions. The mean K values for largemouth bass from Lakes McCloud and Anderson-Cue were 1.00 (n = 3)(McCloud L.) and 1.19 (n = 6)(Anderson-Cue Lake). These values contrast to a K value of 2.17 for largemouth bass in Lake Weir, Florida (mean annual pH 6.5)(Chew 1974), suggesting that the fitness of largemouth bass declines with lake acidification. This trend is not surprising given that aquatic productivity (and thus the food supply of these secondary carnivores) decreases with decreasing pH. Consequently, fish populations may have to rely increasingly on allochthonous organic matter to sustain them (Yamamoto 1972).

The age of individual bass was determined from microscopic examination of scale annuli. The individual fish ranged in age from two to four years old; thus although Anderson-Cue Lake has been acidic ($\text{pH} < 5.0$) for at least the past 10 years (Table 6-2), reproduction of largemouth bass has continued. These data are in contrast to those of Beamish (1976), who found that smallmouth bass (*Micropterus dolomieu*), which is congeneric with largemouth bass, failed to reproduce in Ontario lakes with $\text{pH} < 5.0$ -6.0.

Cronan and Schofield (1979) attributed both the observed gill necrosis and general impoverishment of the fish fauna in acidified Adirondack lakes to increased mobilization of aluminum in the watersheds. Some physical damage to fish has been associated with Al concentrations as low as $100 \mu\text{g/L}$, but the most serious effects have been reported at Al levels above $200 \mu\text{g/L}$. Wright and Snekvik (1978) suggested that increased calcium concentrations may ameliorate the deleterious effects of increased acidity on fish populations by reducing sodium loss from blood. Calcium concentrations generally declined with increasing acidity in the 700 Norwegian lakes they examined. Based on this survey, Wright and Snekvik concluded that fish could be expected in lakes with pH values > 4.5 -5.5 and calcium concentrations > 1 -4 mg/L.

In view of the findings of Cronan and Schofield (1979) for Adirondack fishes, we also examined the gills of the bass for signs of necrosis associated with lake acidification. No evidence of either gill necrosis or of other physical deformities was found in any specimen. The lack of response may reflect differences in water chemistry between Florida lakes and north-temperate lakes of comparable pH, where responses were noted. If fish populations respond more to concentrations of heavy metals and cations than to pH directly, then observations of breeding populations of largemouth bass in Florida at pH values lower than those required by related species in temperate lakes may be explained. The low aluminum concentrations (mean $58 \mu\text{g/L}$) and the moderate calcium levels (mean 1.0 mg/L) found in acidic Florida lakes are conducive to fish reproduction. However, it should be noted that these are preliminary observations, and that further studies are needed on the distribution, fertility and growth of fish in acidic Florida lakes, as well as on the forms and levels of aluminum in the lakes.

REFERENCES

- Adams, D. F., S. O. Farwell, M. R. Pach and W. L. Barnesberger. 1979. Preliminary measurements of biogenic sulfur-containing gas emissions from soils, J. APCA. 29:380-383.
- Ahlberg, M. S., A. C. D. Leslie, J. W. Winchester. 1978. Characteristics of sulfur aerosol in Florida as determined by PIXE analysis. Atmos. Envir. 12:773-777.
- Almer, B., W. Dickson, C. Ekstram, E. Hornström, and U. Miller. 1974. Effects of acidification on Swedish lakes. Ambio 3:30-36.
- American Public Health Association. 1976. Standard methods for the examination of water and wastewater, 14th Ed. A.P.H.A., Washington, D.C.
- Andersson, G., S. Fleischer, and W. Graneli. 1978. Influence of acidification on decomposition processes in lake sediment. Verh. Internat. Verein. Limnol. 20:802-807.
- Aneja, V. P. and A. P. Aneja. 1979. Emission survey of biogenic sulfur from terrestrial surfaces. Presented at Meeting of American Institute of Chemical Engineers, San Francisco, CA., November 25-29.
- Aneja, V. P., J. H. Overton, Jr., L. T. Cupitt, J. L. Durham and W. E. Wilson. 1979. Direct measurements of emission rates of some atmospheric biogenic sulfur compounds. Tellus 31:174-178.
- Barr, A. J., J. H. Goodnight, J. P. Sall, and J. T. Helwig. 1976. A user's guide to statistical analysis system. SAS Institute Inc., Raleigh, NC. 329 p.
- Beamish, R. J. 1974. Loss of fish populations from unexploited remote lakes in Ontario, Canada as a consequence of atmospheric fallout of acid. Water Res. 8:85-95.
- Beamish, R. J. 1976. Acidification of lakes in Canada by acid precipitation and the resulting effects of fishes, pp. 479-498. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State Univ., May 1975, L. S. Dochinger and T. A. Seliga (eds.). U.S. Forest Service Gen. Tech. Rep. NE-23, Upper Darby, PA.
- Beamish, R. J., and H. H. Harvey. 1972. Acidification of the LaCloche mountain lakes, Ontario and resulting fish mortalities. J. Fish Res. Bd. Canada. 29:1131-1143.
- Beamish, R. J., W. L. Lockhart, J. C. Vanloon, and H. H. Harvey. 1975. Long-term acidification of a lake and resulting effects of fishes. Ambio 4:98-102.
- Bell, H. L. 1971. Effects of low pH on the survival and emergence of aquatic insects. Water Res. 5:313-319.

- Bishop, E. W. 1956. Geology and ground-water resources of Highlands County, Florida. Fla. Geol. Surv. Rept. Invest. No. 15. Tallahassee, Fla.
- Bloom, S. A. 1979. Personal Communication. Univ. Florida, Dept. Zoology.
- Bloom, S. A., S. L. Santos, and J. G. Field. 1977. A package of computer programs for benthic community analysis. Bull. Mar. Sci. 27:577-580.
- Bloom, S. A., J. L. Simon and V. D. Hunter. 1972. Animal-sediment relations and community analysis of a Florida estuary. Mar. Biol. 13:43-56.
- Bourne, R. G. (1976) Water Quality effects of sewage effluent on a cypress dome system. M.S. thesis. Univ. Florida, Gainesville, Fla. 121 p.
- Braekke, F. H. (ed). 1976. Impact of acid precipitation on forest and fresh-water ecosystems in Norway. SNSF-project FR 6/76, 1432 Aas-NLH, Norway.
- Bray, J. R., and J. T. Curtis. 1957. An ordination of the upland forest communities of southern Wisconsin. Ecol. Monogr. 27:325-349.
- Brezonik, P. L. 1976. Nutrients and other biologically active substances in atmospheric precipitation. In First Specialty Symposium on Atmospheric Contribution to the Chemistry of Lake Waters, Internat. Assoc. Great Lakes Res. Spec. - Symp. 1: 166-186.
- Brezonik, P. L., E. S. Edgerton, and C. D. Hendry. 1980. Acid precipitation and sulfate deposition in Florida. Science 208:1027-1029.
- Brezonik, P. L., W. H. Morgan, E. E. Shannon, and H. D. Putnam. 1969. Eutrophication factors in north central Florida lakes. Univ. Florida, Eng. Ind. Exper. Sta. Bull. Ser. 133, 101 p.
- Burton, T. M., R. R. Turner, and R. C. Harriss. 1978. Unpublished Results, Florida State University, Tallahassee.
- Byers, H. R. 1974. General meteorology, 4th ed. McGraw-Hill New York.
- Carlisle, V. W., R. E. Caldwell, F. Sodek, L. C. Hammond, F. G. Calhoun, M. A. Granger, and H. L. Breland. 1978. Characterization data for selected Florida soils. Univ. Florida, I.F.A.S., Gainesville, Fla.
- Chapin, J. D. and P. D. Uttormark. 1973. Atmospheric contributions of nitrogen and phosphorus. Tech. Rept. WIS-WRC 73-2, Univ. Wis. Water Res. Center, Madison, Wis.
- Chew, R. L. 1974. Early life history of the Florida largemouth bass. Fish. Bull. 7. Fla. Game Fresh Water Fish Comm., Tallahassee, Fla.
- Clark, W. E., R. H. Musgrove, C. G. Menke, and J. W. Cagle, Jr. 1962. Interim report on the water resources of Alachua, Bradford, Clay and Union Counties, Florida. Fla. Geol. Surv. Inform. Circ. 36. Tallahassee, Fla.

- Clarke, W. E., R. H. Musgrove, C. G. Menke, and J. W. Cagle, Jr. 1963. Hydrology of Brooklyn Lake near Keystone Heights, Florida. Fla. Geol. Surv. Rept. Invest. 33. Tallahassee, Fla.
- Clark, W. E., R. H. Musgrove, C. G. Menke, and J. W. Cagle, Jr. 1964. Water Resources of Alachua, Bradford, Clay, and Union Counties, Florida. Fla. Geol. Surv., Rept. Invest. 35. Tallahassee, Fla.
- Cocke, E. C. 1967. The Myxophyceae of North Carolina. Edwards Brothers, Inc., Ann Arbor, Mich.
- Cogbill, C. V. and G. E. Likens. 1974. Acid precipitation in the north-eastern United States. Wat. Resources Res. 10: 1133-1177.
- Cormack, R. H. 1971. A review of classification. J. Royal Statist. Soc. 134:321-367.
- Costa, H. H. 1967. Responses of Gammarus pulex to modified environment II. Reactions to abnormal hydrogen ion concentrations. Crustaceana 13:1-10.
- Coultas, C. L. 1976. Soils of the Apalachicola National Forest Wetlands. Part I. Titi swamps and savannahs. Soil and crop Sci. Soc. Fla. 36:72-77.
- Coultas, C. L. 1978. The soils of the intertidal zone of Rookery Bay, Florida. Soil Sci. Soc. Amer. J. 42:111-115.
- Coultas, C. L. and E. R. Gross. 1972. Tidal marsh soils of Florida's middle gulf coast. Soil and Crop Sci. Soc. Fla. 37:121-125.
- Cronan, C. S. and C. L. Schofield. 1979. Aluminum leaching response to acid precipitation: Effects on high-elevation watersheds in the northeast. Science 204:304-306.
- Davis, P. and G. W. Osburn. 1969. The pH tolerance of Daphnia pulex. Can. J. Zool. 47:1173-1175.
- Dickson, W. 1978. Some effects of the acidification on Swedish lakes. Verh. Internat. Verein. Limnol. 20:851-856.
- Duchrow, R. M. 1970. Annual progress report for research project F-21-4. Fla. Game Freshwater Fish Comm., Tallahassee, Fla., 39 p.
- Duchrow, R. M. 1971. Annual progress report for project F-21-5. Fla. Game Freshwater Fish Comm., Tallahassee, Fla. 156 p.
- Duchrow, R. M. 1972. Annual progress report for project F-21-6. Fla. Game Freshwater Fish Comm., Tallahassee, Fla. 153 p.
- Dumont, H. J., I. Van De Velde and S. Dumont. 1975. The dry weight estimate of biomass in a selection of Cladocera, Copepoda and Rotifera from the

- plankton, periphyton and benthos of continental waters. *Oecologia* 19 (11):75-97.
- Edmondson, W. T. (ed.). 1959. *Fresh-water biology*. J. Wiley, New York. 1128 p.
- EIFAC (European Inland Fisheries Advisory Committee). 1969. Water quality criteria for European freshwater fish. Report on extreme pH values and inland fisheries. *Water Res.* 3:593-611.
- Eriksson, E. 1960. The yearly circulation of chloride and sulfur in nature: meteorological, geochemical and pedological implications, Part II, *Tellus* 12:63-109.
- Ewel, J. 1979. Univ. Florida, Personal communication.
- Ewel, K. C., J. F. Gamble, and A. E. Lugo. 1976. Aspects of mineral-nutrient cycling in a southern mixed hardwoods forest in north-central Florida. In: *Mineral cycling in southeastern ecosystems*, F. G. Howell, J. B. Gentry, and M. H. Smith (eds.). ERDA Symp. Ser. (Conf.-740513).
- Friend, J. P. 1973. The global sulfur cycle, In: *Chemistry of the lower atmosphere*, S. I. Rasool (ed.). Plenum Press, New York.
- Gaggiani, N. G. and A. G. Lamonds. 1978. Chemical and biological quality of Lakes Faith, Hope and Charity at Maitland, Florida, with emphasis on the effects of storm runoff and bulk precipitation, 1971-74. U.S. Geol. Surv. WRI Open-File Report 77-491. 94 p.
- Galloway, J. N. and G. E. Likens. 1978. The collection of precipitation for chemical analysis. *Tellus* 30:71-82.
- Galloway, J. N., G. E. Likens and E. S. Edgerton. 1976. Acid precipitation in the northeastern United States: pH and acidity. *Science* 194:722-724.
- Galloway, J. N., and Whelpdale. 1980. An atmospheric sulfur model for eastern North America. *Atmos. Envir.* 14:409-417.
- Giddings, J. and J. N. Galloway. 1976. The effects of acid precipitation on aquatic and terrestrial ecosystems. In: *Literature reviews on acid precipitation*. Cornell University Center for Environmental Quality Management, Ithaca, N.Y.
- Gjessing, E. T., A. Henriksen, M. Johannesson and R. F. Wright. 1976. Effects of acid precipitation on freshwater chemistry, pp. 64-85. In: *Impact of acid precipitation on forest and freshwater ecosystems in Norway*. Braekke, F. H. (ed.). SNSF-project FR 6/76, 1432 Aas-NLH, Norway.
- Gorham, E. 1976. Acid precipitation and its influence upon aquatic ecosystems - An overview, pp. 425-458. In: *Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem*, Ohio

- State Univ., May, 1976, L. S. Dochinger and T. A. Seliga (eds.). U.S. Forest Service, Upper Darby, PA.
- Gower, J. C. 1966. A comparison of some methods of cluster analysis. *Biometrics* 22:623.
- Grahn, O. 1976. Macrophyte succession in Swedish lakes caused by deposition of airborne acid substances. pp. 519-530 In: *Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem*. 1975, L. S. Dochinger and T. A. Seliga (eds.). U.S. Forest Service, Upper Darby, PA.
- Granat, L. 1972. On the relationship between pH and the chemical composition in atmospheric precipitation. *Tellus* 24:550-560.
- Granat, L., H. Rodhe and R. O. Hallberg. 1976. The global sulfur cycle, pp. 89-134. In: *Nitrogen, phosphorus and sulfur global cycles*, B. H. Svensson and R. Söderlund (eds.). *Scope Report 7. Ecol. Bull.* 22, (Stockholm).
- Hagen, A. and A. Langeland. 1973. Polluted snow in southern Norway and the effect of the meltwater on freshwater and aquatic organisms. *Environ. Poll.* 5:45-57.
- Harp, G. L., and R. S. Cambell. 1967. The distribution of Tendipes plumosus (Linne') in mineral acid water. *Limnol. Oceanogr.* 12:260-264.
- Hendrey, G. R., K. Baalstud, T. S. Traaen, M. Laake, and G. Raddum. 1976. Acid precipitation: some hydrobiological changes. *Ambio* 5:224-227.
- Hendry, C. D. 1977. The chemistry of precipitation in north-central Florida. M.S. thesis. University of Florida, Gainesville, Fla., 141 p.
- Hendry, C. D. and P. L. Brezonik. 1980. Chemistry of precipitation at Gainesville, Florida. *Env. Sci. Technol.* 14:843-849.
- Hennessey, W. K. and D. E. Holcomb. 1967. Annual progress report for research project F-21-R-1. Fla. Game and Fresh Water Comm. Tallahassee, Fla. 15 p.
- Hitchcock, D. R. 1975. Dimethyl sulfide emissions to the global atmosphere, *Chemosphere* 3:137-138.
- Holcomb, D. E. 1968. Annual progress report for research project F-21-R-1. Fla. Game Freshwater Fish Comm. Tallahassee, Fla., 105 p.
- Holcomb, D.E. 1969. Annual progress report for research project F-21-3. Fla. Game Freshwater Fish Comm. Tallahassee, Fla. 77 p.
- Holcomb, D. E. and C. Starling. 1973. Final completion report for project F-21-7. Fla. Game Freshwater Fish Comm., Tallahassee, Fla., 107 p.

- Hornbeck, J. W., G. E. Likens, and J. S. Eaton. 1976. Seasonal patterns in acidity of precipitation and their implications for forest stream ecosystems, pp. 597-610. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem. Ohio State Univ., May, 1975, L. S. Dochinger and T. A. Seliga (eds.). U.S. Forest Service. Upper Darby, PA.
- Hultberg, H. 1976. Thermally stratified acid waters in late winter - A key factor inducing self-accelerating processes which increase acidification, pp. 503-518. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem. U.S. Forest Service.
- Hutchinson, T. C. and M. Havas. 1979. Response of aquatic invertebrates to acid stress. Presented at Div. Environ. Chem., 178th Nat. Meet. Amer. Chem. Soc., Washington, DC.
- Jaeschke, W. 1978. New methods for the analysis of SO_2 and H_2S in remote areas and their application to the atmosphere. Atmos. Envir. 12:715-721.
- Jordan, H. V., C. E. Bardsley, Jr., L. E. Ensminger and J. A. Lutz, Jr. 1959. Sulfur content of rainwater and atmosphere in southern states as related to crop needs, U.S.D.A. Tech. Bull. #1196.
- Joyner, B. F. 1971. Appraisal of chemical and biological conditions of Lake Okeechobee, Florida, 1969-70. U.S. Geol. Surv. Open. File Rept. 71006. Tallahassee, Fla. 90 p.
- Junge, C. E. 1958. The distribution of ammonia and nitrate in rain water over the United States. Trans. Am. Geophys. Union 39:241-248.
- Junge, C. E. and R. T. Werby. 1958. The concentration of chloride, sodium, potassium, calcium and sulfate in rainwater over the United States. J. Meteorology. 15:417-425.
- Kellogg, W. W., R. D. Cadle, E. R. Allen, A. L. Lazrus and E. A. Martell. 1972. The sulfur cycle. Science 175:587-595.
- Kroes, H. W. 1971. Growth interactions between Chlamydomonas globosa (Snow) and Chlorococcum ellipsoidicum (Deason and Bold) under different experimental conditions, with special attention to the role of pH. Limnol. Oceanogr. 16:869-880.
- Lackey, J. B. 1938. The flora and fauna of surface waters polluted by acid mine drainage. Public Health Reports 53:1499-1507.
- Lamonds, A. G. and Merritt. 1976. Proposed Cross-Florida Barge Canal: Water quality aspects with a section on waste-assimilative capacity. U.S. Geol. Survey, Water Resources Inv. 76-23.
- Leivestad, H., G. Hendrey, I. P. Muniz, and E. Snekvik. 1976. Effects of acid precipitation on freshwater organisms. In: Impact of Acid

- Precipitation on Forest and Freshwater Ecosystems in Norway. FR 6/76. 87-111. SNSF-project. 1432 Aas-NLH, Norway.
- Likens, G. E. 1972. The chemistry of precipitation in the central Finger Lakes region. Cornell Univ. Water Resour. Mar. Sci. Center, Ithaca, NY. Tech. Rept. 50.
- Likens, G. E. 1976. Acid precipitation, Chem. Eng. News 54(48):29-44.
- Likens, G.E., F. H. Bormann, R. S. Pierce, J. S. Eaton and N. M. Johnson. 1977. Biogeochemistry of a Forested Ecosystem. Springer Verlag, New York.
- Likens, G. E., R. F. Wright, J. N. Galloway and T. J. Butler. 1979. Acid rain, Scientific American 241:43-51.
- Lodge, J. P. Jr., K. C. Hill, J. B. Pate, E. Lorange, W. Basbergill, A. L. Laxrus, and G. S. Swanson. 1968. Chemistry of United States precipitation. Final report on the national precipitation sampling network. Laboratory of Atmospheric Sciences, National Center for Atmospheric Res. Boulder, Colorado. 66 p.
- Madsen, B. 1979. Univ. Central Florida, Orlando, personal communication.
- Mahadevan, S., J. B. Murdock, F. S. Reeves, J. K. Culter, R. A. Lotspeich and J. D. Murdoch. 1977. Benthic Studies chapter four: In Tampa Electric Company final report on the Big Bend thermal and ecological surveys. Conservation Consultants, Inc, Palmetto, Fla.
- Malmer, N. 1976. Acid Precipitation: Chemical changes in the soil. Ambio. 5:231-234.
- Maroulis, P. J. and A. R. Bandy. 1976. Estimate of the contribution of biologically produced dimethyl sulfide to the global sulfur cycle. Science 196:647-648.
- Mattraw, H. C. and C. B. Sherwood. 1977. Quality of storm-water runoff from a residential area, Broward County, Florida. Jour. Res. U.S. Geol. Surv. 5:823-834.
- Messer, J. J. and P. L. Brezonik. 1980a. Regional nitrogen mass balance model for the Florida peninsula, In: Biogeochemistry of ancient and modern environments, Proc. Fourth Internat. Symp. Environ. Biogeochem., Canberra, Australia, August, 1979. Australian Acad. Sci., Canberra.
- Messer, J. J. and P. L. Brezonik. 1981. Importance of atmospheric fluxes to the nitrogen mass balance of lakes in the Florida peninsula, pp. 217-236 In: Atmospheric pollutants in natural waters, S. J. Eisenreich, ed., Ann Arbor Science Publ.

- Milleson, J. F. 1978. Limnological investigations of seven lakes in the Istokpoga drainage basin. S. Fla. Water Manag. Dist., W. Palm Beach, Fla. 102 p.
- Moss, B. 1973. The influence of environmental factors on the distribution of freshwater Algae: An experimental study. IV. Growth of test species in natural lake waters, and conclusions. J. Ecol. 61:193-211.
- Nikolsky, G. V. 1963. The ecology of fishes. Academic Press London and New York. 352 p.
- Odén, S. 1976. The acid precipitation problem - an outline of concepts. pp. 1-36. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State Univ., May, 1975, L. S. Cochinger and T. A. Seliga (eds.). U.S. Forest Service, Upper Darby, PA.
- Økland, J. 1969. Distribution and ecology of the freshwater snails (Gastropoda) of Norway. Malacologia 9:143-151.
- Overrein, L. N. 1976. A presentation of the Norwegian project. "Acid Precipitation - Effects on Forest and Fish", pp. 37-42. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State Univ., May, 1975, L. S. Cochinger and T. A. Seliga (eds.). U.S. Forest Service, Upper Darby, PA.
- Packer, R. K. and W. A. Dunson. 1970. Effects of low environmental pH on blood pH and sodium balance of brook trout. Exp. Zool. 174:65-72.
- Parsons, J. D. 1968. The effects of acid strip-mine effluents on the ecology of a stream. Arch. Hydrobiol. 65:25-50.
- Parsons, J. D. 1976. Effects of acid-mine wastes on aquatic ecosystems. pp. 571-596. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State Univ., May, 1975, L. S. Cochinger and T. A. Seliga (eds.). U.S. Forest Service, Upper Darby, PA.
- Pennak, R. W., 1953. Fresh-water invertebrates of the United States. Ronald Press, New York. 769 p.
- Pielou, E. C. 1969. An introduction to mathematical ecology. J. Wiley, New York.
- Poole, R. W. 1974. An introduction to quantitative ecology. McGraw-Hill, New York.
- Powers, C. F. and A. Robertson. 1967. Design and evaluation of an all-purpose benthos sampler. Great Lakes Res. Div. Univ. Mich. Spec. Rept. 30:126-133.

- Prescott, G. W. 1954. How to know the fresh-water algae. W. C. Brown Publ., Dubuque, Iowa. 272 p.
- Roth, J. C. 1968. Benthic and limnetic distribution of three *Chaoborus* species in a southern Michigan lake (Diptera, Chaoboridae). *Limnol. Oceanogr.* 13:242-247.
- Sanders, H. L. 1968. Marine benthic diversity: A comparative study. *Amer. Natur.* 102:253-247.
- Schneider, R. F. and J. A. Little. 1969. Characterization of bottom sediments and selected nitrogen and phosphorus sources in Lake Apopka, Florida. U.S. Dept. of Interior Report, F.W.P.C.A., Southeast Water Lab., Athens, Ga. 127 p.
- Schofield, C. L. 1976. Lake acidification in the Adirondack mountains of New York: Causes and consequences, pp. 477-478. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State Univ., May, 1975, L. S. Dochinger and T. A. Seliga (eds.). U.S. Forest Service, Upper Darby, PA.
- Schofield, C. L. 1979. Acidification impacts on fish populations. Presented at Div. Environ. Chem., 178th Nat. Meet. Amer. Chem. Soc., Washington, D.C.
- Shannon, E. E. 1970. Eutrophication-trophic state relationships in north-central Florida lakes. Ph.D. thesis, Univ. Florida, Gainesville, Fla. 257 p.
- Shannon, E. E., and P. L. Brezonik. 1972. Limnological characteristics of north and central Florida lakes. *Limnol. Oceanogr.* 17:97-110.
- Simpson, E. H. 1949. Measurement of diversity. *Nature* 163:688.
- Smith, F. B., R. G. Leighty, R. E. Caldwell, V. W. Carlisle, L. G. Thompson, Jr. and T. C. Mathews. 1973. Principal soil areas of Florida, a supplement to the general soil map, Bull #717. Univ. Florida, I.F.A.S., Gainesville, Fla.
- Smith, G. M., 1950. The fresh-water algae of the United States. McGraw-Hill, New York. 719 p.
- Sneath, P. A., and R. R. Sokal. 1973. Numerical taxonomy. Freeman and Co., San Francisco. 573 p.
- Sprules, W. G. 1975. Midsummer crustacean zooplankton communities in acid-stressed lakes. *J. Fish. Res. Bd Can.* 32:389-395.
- Stainton, M. P. 1974. Simple, efficient reduction column for use in the automated determination of nitrate in water. *Anal. Chem.* 46:1616.
- Stokes, P. M. and T. C. Hutchinson. 1976. The effects of acid particulate precipitation on phytoplankton and lake chemistry in the Sudbury region

- of Ontario, Canada, pp. 499-500. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State Univ., May, 1975, L. S. Dochinger and T. A. Seliga (eds.). U.S. Forest Service, Upper Darby, PA.
- Tatera, B. S. 1970. Parameters which influence fluoride emissions from gypsum ponds. Ph.D. thesis. Univ. Florida. Gainesville, Fla.
- Tomkiewicz, S. M. and W. A. Dunson. 1976. Aquatic insect diversity and biomass in a stream marginally polluted by acid strip mine drainage. *Water Res.* 11:397-402.
- U.S. Environmental Protection Agency. 1976. Methods for chemical analysis of water and wastes. National Environmental Research Center, Cincinnati, Ohio, EPA-625/6-74-003a. 298 p.
- Varian. 1973. Instruction Manual for Models 1100 and 1200 Atomic Absorption Spectrophotometers. Varian Techtron PTY. LTD. Melbourne, Australia.
- Vollenweider, R. A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication. Org. Economic Cooperation and Development, Paris. Report DAS/CSL/68.27.
- Vollenweider, R. A. 1975. Input-output models with special reference to the phosphorus loading concept in limnology. *Schweiz. Z. Hydrol.* 37:53-84.
- Weber, C. I. 1971. A guide to the common diatoms at water pollution surveillance system stations. U.S. Environmental Protection Agency, Cincinnati, Ohio. 100 p.
- Wetzel, R. G. 1975. Limnology. W. B. Saunders Co., Philadelphia.
- Whitford, L. A. and G. J. Schumacher. 1968. A manual of the freshwater algae in North Carolina. Bull. 188, N.C. Ag. Exp. Sta. Raleigh, NC. 324 p.
- Wisniewski, J. and W. R. Cotton. 1974. Chemical analysis of south Florida's environment. In: Precipitation scavenging, R. G. Semonin and R. W. Beadle, (Eds.). Technical Information Center, ERDA. Springfield, Vir.
- Wright, R. F. 1976. Acid precipitation and its effects on freshwater ecosystems: An annotated bibliography, pp. 619-680. In: Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem, Ohio State Univ., May, 1975, L. S. Dochinger and T. A. Seliga (eds.). U.S. Forest Service, Upper Darby, PA.
- Wright, R. F. and E. Snekvik. 1978. Acid Precipitation: Chemistry and fish populations in 700 lakes in southernmost Norway. *Verh. Internat. Verein. Limnol.* 20:765-775.

- Yamamoto, G. 1972. Trophic structure in lake Totsu-numa, an acidotrophic lake in Japan, with special reference to the importance of the terrestrial community. In: Productivity Problems of Freshwaters. Z. Kajak & A. Hillbricht-Ilkouska. (eds.). PWN, Polish Scientific Publishers, Warsaw.
- Yan, N. D. 1975. Acid precipitation and its effects on phytoplankton communities of Carlyle Lake, Ontario. M.S. thesis, Univ. Toronto, Toronto, Ont. 116 p.
- Yan, N. D. 1979. Crustacean zooplankton communities of acidic, metal-contaminated lakes near Sudbury, Ontario. Presented at Div. of Envir. Chem., 178th Nat. Meet., Amer. Chem. Soc. Washington, D.C.
- Yan, N. D., and P. Stokes. 1978. Phytoplankton of an acidic lake, and its responses to experimental alterations of pH. Environ. Conservation 5:93-100.

APPENDIX 1

Analytical Methods for Chemical and Physical Parameters on Rain and Lake Samples.

Parameter	Method	Reference
pH	Orion Model 801 Ionalyzer in the lab. An Orion Model 401 Ionalyzer in the field.	
Conductivity	Beckman Model RC 16B2 conductivity bridge.	APHA (1976)
Dissolved Oxygen	YSI Model 51A Oxygen Meter, Hydrolab Monitor, or Winkler wet chemical technique.	APHA (1976)
Temperature	YSI Model 51A Oxygen Meter or Hydrolab Monitor.	
Color	Sample centrifuged and compared against standard chloroplatinate solution at 420 nm on a Bausch and Lomb Spectronic 89.	APHA (1976)
Turbidity	Bach Turbidimeter Model 2424 standardized with formazin suspensions.	APHA (1976)
Alkalinity	Titration with standard acid using color indicators.	APHA (1976)
Total Kjeldahl Nitrogen (TKN)	Manual semi-micro digestion followed by analysis of ammonium on neutralized samples by alkaline phenol method on AutoAnalyzer.	EPA (1974)

Parameter	Method	Reference
Ammonium	Alkaline phenol method on AutoAnalyzer.	EPA (1974)
Nitrate	Cadmium (wire) reduction method on AutoAnalyzer.	Statton (1975)
Total Phosphorus	Sample digested with ammonium persulfate, and measured using the single reagent molybdenum blue test on an unfiltered sample.	APIA (1976)
Orthophosphate	Measured at 880 nm using the molybdenum blue test on a filtered sample.	APIA (1976)
Total Inorganic and Organic Carbon	Measured by combusting samples in a Beckman Model 915 TOC Analyzer with analysis in a Beckman Model 865 Infrared Analyzer. TC - IC = OC.	APIA (1976)
Silica	Molybdenum blue method on Technicon AutoAnalyzer. (Analogous to manual method in APIA 1975).	Technicon Method #186-728
Sulfate	Methylthymol blue method on Technicon AutoAnalyzer.	APIA (1976)
Chloride	Ferricyanide method on Technicon AutoAnalyzer.	APIA (1976)
Aluminum	Eriochrome Cyanine R Method on Technicon AutoAnalyzer.	APIA (1976)
Fluoride	Orion Model 96-09 Specific Ion Electrode	APIA (1976)
Cations (Calcium, Magnesium, Sodium, Potassium)	Varian Model 1200 atomic absorption spectrophotometer.	EPA (1974)

APPENDIX II

Volume-weighted mean concentrations and Annual Deposition Rates for each site during the project period.

APPENDIX KEY

RAIN	=	Rainfall (cm)
PH	=	-Log [a _H ⁺] (unitless)
CON	=	Specific conductance (uS/cm @25°C)
NA	=	Sodium (mg/L)
K	=	Potassium (mg/L)
MG	=	Magnesium (mg/L)
CA	=	Calcium (mg/L)
NH4	=	Ammonium nitrogen (mg/L)
NO3	=	Nitrate nitrogen (mg/L)
SO4	=	Sulfate (mg/L)
CL	=	Chloride (mg/L)
OP	=	Ortho-phosphorus (mg/L)
TP	=	Total phosphorus (mg/L)
TKN	=	Total Kjeldahl nitrogen (mg/L)
H	=	Hydrogen ion (g/L)
ORGN	=	Organic nitrogen (mg/L)
ORGP	=	Organic phosphorus (mg/L)
INORGN	=	Inorganic nitrogen (mg/L)
TOTN	=	Total nitrogen (mg/L)
UEOH	=	Microequivalents hydrogen ion (ueq/L)
EOHDEP	=	Hydrogen deposition (g/ha-yr)
SES04	=	Sea (Marine-derived) sulfate (mg/L)
EXS04	=	Excess (non-marine) sulfate (mg/L)
SESDEP	=	Sea sulfate-sulfur deposition (kg/ha-yr)
EXSDEP	=	Excess sulfate-sulfur deposition (kg/ha-yr)
SO4DEP	=	Sulfate deposition (kg/ha-yr)
NADEP	=	Sodium deposition (kg/ha-yr)
KDEP	=	Potassium deposition (kg/ha-yr)
MGDEP	=	Magnesium deposition (kg/ha-yr)
CADEP	=	Calcium deposition (kg/ha-yr)
NH4DEP	=	Ammonium nitrogen deposition (kg/ha-yr)
NO3DEP	=	Nitrate nitrogen deposition (kg/ha-yr)
CLDEP	=	Chloride deposition (kg/ha-yr)
OPDEP	=	Ortho-phosphorus deposition (kg/ha-yr)
TPDEP	=	Total phosphorus deposition (kg/ha-yr)
TKNDEP	=	Total kjeldahl nitrogen deposition (kg/ha-yr)
TNDEP	=	Total nitrogen deposition (kg/ha-yr)
ORGNDEP	=	Organic nitrogen deposition (kg/ha-yr)
ORGPDEP	=	Organic phosphorus deposition (kg/ha-yr)
INNDEP	=	Inorganic nitrogen deposition (kg/ha-yr)

1978 PRECIPITATION CONCENTRATIONS AND DEPOSITIONS

A. Average annual volume-weighted

[illegible][illegible]

C. Volume-weighted concentrations and total deposition over the two-year period, 1978 and 1979

[illegible]

D. Volume-weighted average concentrations and annual depositions for the period May 1, 1978 to April 30, 1979

SITE	DATE	HA	PH	CUN	NA	K	MO	CA	NH	NO	SO	C	DP	TP	TN	ORON	OROL
APOKA WET	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
BAHIA HONDA KEY	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
BELLE GLADE WET	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
BRADENTON	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
BRONSON	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
CEDAR KEY BULK	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
CEDAR KEY WET	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
CHIPLEY	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
CLENTON SHARP BULK	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
CORT MYERS	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
GAINESVILLE BULK	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
GAINESVILLE WET	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
HASTINGS	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
JACKSONVILLE	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
JASPER	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
JAY	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
LAKE ALFRED	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
LAKE PLACID	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
LISBON	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
MARTIN LUTHER FARMS	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
MARTIN LUTHER	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
MIAMI	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
STUART	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
TALLAHASSEE	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
WALDO BULK	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
WALDO THROUGHFALL	78-79	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120